TEXTILE RESEARCH JOURNAL

VOLUME XIX December, 1949 *NUMBER 12*

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE, INC.

AND

THE TEXTILE FOUNDATION

Editorial Office: 10 East 40th Street, New York 16, N. Y.

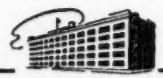
THE NEW MIRACLE "EYE" IN TEXTILE RESEARCH...

Radioactive Isotopes

Radioactive Isotopes . . . a practical application of atomic energy . . . are now being employed in Textile Research by the United States Testing Company, Inc. In a scientifically controlled laboratory, under the supervision of specially trained technicians, textile researches never before possible are now part of a regular program. Here are a few examples:

- *Determining maximum absorption in dyestuffs.*
- *Controlling the concentration in dye baths.*
- *Measuring the efficiency of water repellent substances quantitatively.*
- *Controlling the uniformity of coatings on fabrics during processing.*
- *Study of intermediate reactions in the manufacture of dyestuffs.*
- *Eliminating static conditions in mills.*
- *Measuring the distribution of lubricants on synthetic yarn.*
- *Keeping the coagulating and desulphurizing baths within pre-determined concentration ranges in the manufacture of rayon.*
- *Tracing the cause of "cratering" of spinnerets in rayon manufacture.*
- *Controlling the film gauge of sheet plastic to within one hundred-thousandth of an inch.*
- *Study of friction loss of textiles to one hundred-thousandth of an inch.*
- *We are now in the process of manufacturing radioactive thickness gauges for plant installation for determining the uniformity of thickness or coating of materials.*

If you are faced with a textile problem that seemingly defies solution, write and we will arrange for a consultation. If the problem can be solved with Radioactive Isotopes, we will outline procedure and cost without obligation on your part.



Radioactive Isotopes Laboratory

UNITED STATES TESTING COMPANY, INC.

Established 1880

HOBOKEN, NEW JERSEY

PHILADELPHIA, PA. • BOSTON, MASS. • WOONSOCKET, R. I.
CHICAGO, ILL. • NEW YORK, N. Y. • LOS ANGELES, CAL.
DENVER, COL. • MEMPHIS, TENN.

Member of American Council of Commercial Laboratories

TEXTILE RESEARCH JOURNAL

VOL. XIX, No. 12 December, 1949

In This Issue

Cellulose Studies

XIII: The Heterogeneous Hydrolysis of Trimethyl Cellulose

XIV: The Fractionation and Solubility of Trimethyl Cellulose

XV: Infrared Spectra of Trimethyl Cellulose, Cellulose, and Starch

Richard Steele and Eugene Pacsu 771

The Preparation and Properties of Alkali-Soluble Metal Carboxymethylcellulose Fibers — J. David Reid and George C. Daul 794

Note on the Disintegration of Wool in Abrasion Tests — Herbert F. Schiefer and John F. Krasny 802

The Flow Properties of Fibers — Stephen A. Rossmassler and Henry Eyring 810

INDUSTRIAL SECTION

The Structure of the Wool Fiber — Giles E. Hopkins 816

Direct Steam-Injection Continuous Starch-Cooker — L. W. Rainard and G. Zanolli 822

Selection of a Temperature-Measuring System for Textile Mills — C. W. Bowden, Jr. 826

Laboratory Techniques: New Methods for Holding Multi- and Single-Filament Tensile Specimens — Richard LaTorre and Waller George 830

Letters to the Editor: Dry Needle Cooling in Heavy-Duty and High-Speed Machine Sewing Operations — H. F. Hume and T. O. Lee 833

Book Reviews 835

Abstracts 839

Editor: Julian S. Jacobs *Managing Editor:* Julia M. Crisp

Associate Editors

H. J. Ball, Earl E. Berkley, Henry Eyring, Gustavus J. Esselen, Earl K. Fischer, Milton Harris, K. L. Hertel, H. Mark, E. R. Schwarz, Kyle Ward, Jr.

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is the official publication of Textile Research Institute, Inc., and the Textile Foundation.

Manuscripts and communications should be sent to the editorial offices, 10 East 40th Street, New York 16, N. Y.

Subscription rates: General—$15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Special—$10.00 per year for United States and Canadian students, teachers, educational institutions, public libraries, governmental libraries and departments, plus 50 cents for postage to Canada. Single copies, $1.50 each.

Entered as second-class matter, April 27, 1945, at the postoffice at Lancaster, Pa., under the Act of August 24, 1912.

Contents copyrighted 1949 by Textile Research Institute, Inc.

Advertising rates supplied on request.

Woolfacts

THE WOOL BUREAU is devoted to the interests of apparel wool in North America. It serves consumers, retailers, manufacturers and educators, and it constantly encourages the use of wool by means of promotion, education and research.

Four-Point Program

Objectives of the Bureau's technical program are four-fold:

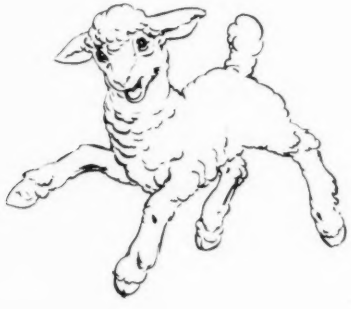
1. Analysis of consumer requirements and manufacturing problems.
2. Stimulation of research which will show how these requirements and problems can be satisfied.
3. Interpretation of research results in terms of mill processes and product design.
4. Assistance to individual mills in the application of improved engineering and technology.

Technical Department

Through its Technical Department, the Bureau maintains close liaison with wool textile mills, government and private research laboratories and technical trade associations. Recently it began the publication of "Newsletter for Wool Textile Executives" to bring significant research information to the attention of mill executives and technologists and thereby help to bridge the gap between the laboratory and mill management.

Help to Mills

During the coming year, The Wool Bureau will especially strive to assist those mills who wish to initiate or expand a small engineering development or control program. *Such mills are invited to write Giles E. Hopkins, Technical Director, The Wool Bureau, Inc., New York 19, N. Y.*



Technical Department

THE WOOL BUREAU, INCORPORATED

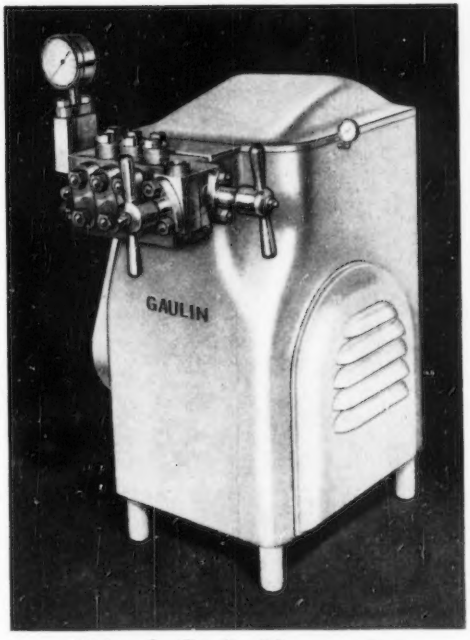
16 West 46th Street, New York 19, N.Y.

THE GAULIN TEXTILE HOMOGENIZER

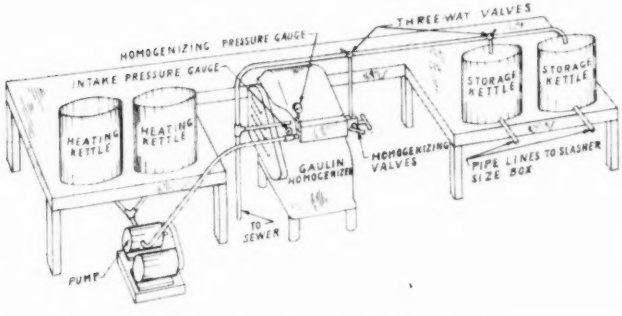
The Gaulin Homogenizer is the result of years of continuous research and development by the oldest and largest manufacturer of this type of equipment in the country. The Model TE, a rugged, heavy-duty machine designed especially for the textile industry, is manufactured in capacities ranging from 100 to 2,000 gallons per hour. It is the most efficient Homogenizer made, and is easily maintained in top running condition.

•

Construction is compact and sturdy.
All machines are factory-tested.
Highest-quality materials are used.



100 gal. Gaulin Homogenizer



Installation of a Gaulin Homogenizer can be made very easily in any textile mill. No major changes in plant layout are required, and the machine can usually be installed without interrupting production.

The illustration (left) shows a typical installation plan in a textile mill. Experience has taught that a layout similar to this insures best results and maximum service from the Homogenizer.

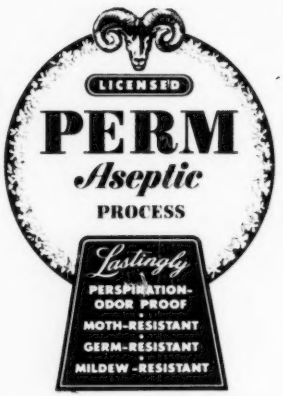
MANTON GAULIN
Manufacturing Company, Inc.

•

44 Garden Street
Everett 49, Mass.

Mill Efficiency

Microorganisms are responsible for a loss of efficiency in processing. Recent investigations under actual conditions of use have convinced us that microbiological destruction of cotton fibers is as much as 10% in the bale. This figure jumps to 20% when fibers in the fabric are examined.

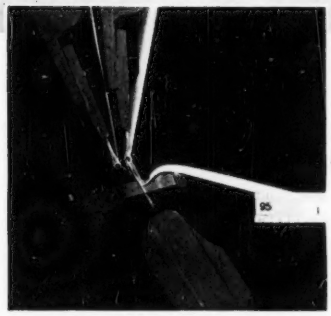


Considerable time lost due to breaks during processing can be avoided if cotton is treated with PERM-*Aseptic*. The advantages thus obtained are far greater than the cost of PERM-*Aseptic*.

PERM-*Aseptic* CORPORATION

432 WAVERLY AVE. MAMARONECK, N. Y.

Dr. Edward Abrams, for six years Head of the Microbiological Laboratory at the National Bureau of Standards, Washington, D.C., and for the past three years Head of the Biology Division of the Institute of Textile Technology, Charlottesville, Va., has been retained by the PERM-*Aseptic* Corporation to assist the textile industry in applying PERM-*Aseptic* to specific mill problems. For further information, please contact Dr. Abrams, who is Director of Research of Laboratories Research, 40 Worth Street, New York 13, N. Y.



Single-flash STROBOLUME picture of a warp knitter (side-view)

The STROBOLUME normally is housed in the power-supply case. Complete, it weighs only 18½ pounds. The sealed-beam lamp and its case are removable from the supply assembly for use at the end of a 10-foot cable. The lamp housing is equipped with a standard tripod socket.

TYPE 1532-A STROBOLUME . . . $225.00

TYPE 631-BS18 STROBOTAC
(Special, with speed range of 60 to 14,400 rpm.) **$170.00**

and *NOW* . . . An EXTRA-HIGH-INTENSITY STROBOSCOPE for S-l-o-w Motion Textile Machinery

ESPECIALLY designed for the textile field, the new Type 1532-A STROBOLUME furnishes just the right light intensity and slow flashing rate for either observing or photographing loom shuttle operation, warp knitters and the many other s-l-o-w speed textile machines.

The STROBOLUME gives an intense light with a flash duration of only *ten millionths* of a second. It can be operated in several ways. For single-flash pictures, taken at random, it is equipped with a cord and push-button switch to fire the light in a single flash. For multiple flash pictures or visual observation, a contactor on any rotating shaft of the machine will supply flashes synchronized to 1200 rpm.

A special slow-speed STROBOTAC is available for use with the STROBOLUME to fire the latter at any speed between 60 and 1200 rpm. This special STROBOTAC, alone, has a speed range of 60 to 14,400 rpm.

The new STROBOLUME opens up many new possibilities in the scientific and most efficient operation, maintenance and design of slow-speed textile equipment. If you have ANY motion-study problem in the use or modification of your machines, the STROBOLUME may be an invaluable aide

This equipment is sold directly from our factory. We do not have any travelling salesmen. May we send you literature?

WRITE FOR THE STROBOLUME BULLETIN

GENERAL RADIO COMPANY Cambridge 39, Massachusetts

90 West St., New York 6 920 S. Michigan Ave., Chicago 5 1000 N. Seward St., Los Angeles 38

SERC YARN EVENNESS TESTING *with* ELECTRON MICROMETER

MEASURES

❖

RECORDS

❖

COUNTS

❖

ANALYZES

❖

YARN EVENNESS

❖

Illustration shows YARN ANALYSER, EMD-8 (Console Model). Equipment includes eight counting units . . . each counter can be set independently . . . counter data gives frequency distribution of yarn variation.

Every type of yarn . . . from synthetics to jute . . . all can be measured on the SERC ELECTRON MICROMETER.

Independent of moisture conditions . . . insensitive to blend variations . . . models available for recording, counting, and automatic analysis.

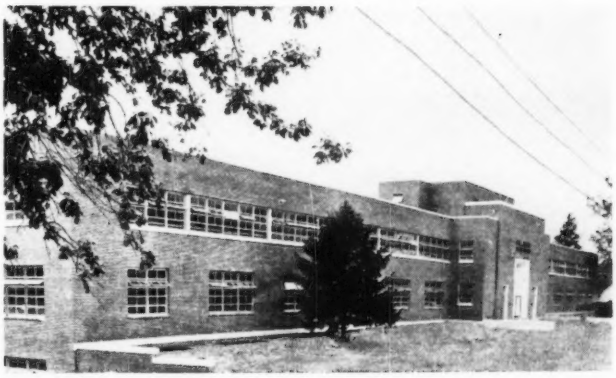
Choice of models . . . from automatic integrating and analyzing units . . . to portable, hand-carried instruments for actual, in-process measurement and control . . . right on the spinning frame.

Write today for additional data to Dept. R

STANDARD ELECTRONICS RESEARCH CORPORATION

Two East End Ave. . . New York 21, N. Y.

Shown at right is the main building on Philadelphia Textile Institute's new 12-acre campus. Other buildings already built—the Administrative Mansion and the Hesslein Library. To be erected—dormitories, gymnasium and auditorium.



THE PHILADELPHIA TEXTILE INSTITUTE

America's Pioneer Textile School

OFFERS

1. College-level, four-year courses leading to the degree of Bachelor of Science in Textile Engineering. Students may elect to specialize either in manufacture of textile yarns and fabrics or in dyeing and finishing of textile materials.

2. Diploma courses, three years in length, providing opportunity for thorough study of textile technology but without the additional courses necessary for earning the degree.

3. Short-term courses designed to offer students intensive training in some one phase of textile manufacture and/or processing, and leading to a Certificate of Proficiency.

4. Ideal facilities and equipment for carrying out specific research projects for industry and government on a careful, competent and comprehensive basis, at modest cost.

For a Sound Investment in Future Profits—
Send the BEST young men in your organization to

Philadelphia Textile Institute

Philadelphia 44, Penna.

Address The Director for Full Details

READ . . .

The Textile Engineer

Official publication of the Alumni Association of Philadelphia Textile Inst.

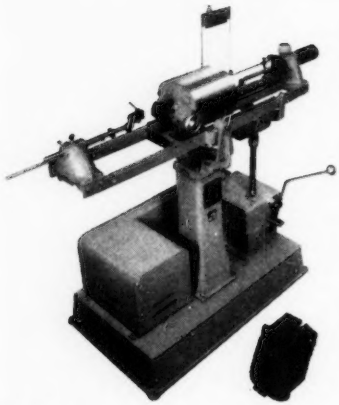
Published Quarterly

Subscription: $1.00 per year

Scott Testers present at T.R.I.

ANNUAL MEETING DECEMBER, 1949

Latest Models



MODEL IP Incline-plane, the most convenient form of constant rate of load tester for tensile and hysteresis. Sufficiently accurate for a laboratory tool, yet sturdily built for production.

MODEL J Standard of the Industry for many years for tensile testing of fabric; yarn in single end or skein; cord and twine; also may be equipped for ball burst test. Capacities up to 500 lbs. tensile.

WE INVITE **TESTED IS TRUSTED** YOUR INQUIRIES

SCOTT TESTERS, INC., 145 BLACKSTONE ST., PROVIDENCE, R. I.

Scott Testers — Standard of the World

TEXTILE RESEARCH JOURNAL

VOL. XIX, NO. 12 December, 1949

Cellulose Studies*

XIII. The Heterogeneous Hydrolysis of Trimethyl Cellulose

Richard Steele and Eugene Pacsu

Contribution from the Textile Foundation and Frick Chemical Laboratory, Princeton University

EARLY INVESTIGATIONS of the heterogeneous acid hydrolysis of cellulose [13] were directed toward increasing the yield of alcohol which could be produced by fermentation of the "inversion" products of cellulose. However, more recently several investigators have studied this degradation under such mild conditions that the fiber structure was retained, and have related their results to the course of the reaction and to the chemical and morphological structure of the fiber.

Eisenhut and Schwartz [4] treated various native, mercerized, and regenerated celluloses with 1N HCl at 35°–45°C and followed the degradation by viscosimetric measurements of the degree of polymerization in cuprammonium solution. They found that such a heterogeneous hydrolytic degradation did not proceed at a constant rate, but that there was a slowing down with time. They attributed the slowing down of the reaction to the rapid formation in localized attack areas of very short cellulose chains which inhibited further reaction. Treatment of the partially degraded material with alkali made it again susceptible to rapid attack which, in turn, slowed down as before. This was presumably caused by the removal of the short chains by the alkali treatment. These investigators also observed that pretreatment with sodium hydroxide increased the velocity of hydrolysis.

Husemann and Schulz [12] investigated the heterogeneous degradation of cellulose in potassium bisulfate solutions, following the change in chain length by viscosity and osmotic pressure measurements. The D.P.'s calculated by these two methods made it possible to calculate the homogeneity of the chain lengths in the degraded material. The observed values did not agree with the results to be expected from random hydrolysis, and this disagreement led to the proposal of a periodic structure for cellulose.

Mehta and Pacsu [11] observed the hydrolysis of native cellulose and viscose rayon in 10% aqueous lactic acid and in an aqueous mixture containing 10% acetic acid and 10% sodium chloride. The

* The first paper in this series appeared in the October, 1945, issue of TEXTILE RESEARCH JOURNAL. Papers II–VIII were published in March, April, June, July, August, October, and November, 1946. Paper IX appeared in the August, 1947, issue, X in July, 1948, XI in October, 1949, and XII in November, 1949. Papers XIV and XV follow XIII in this issue.

course of the reaction was again followed by measuring viscosimetrically the D.P. in cuprammonium solution. They found an initial rapid hydrolysis for native cellulose down to a D.P. of about 260, proceeding with a rate constant of 3.43×10^{-3} at 97°C, which is much higher than the constant for the hydrolysis of 1,4-glycosidic bonds under similar conditions. After the hydrolysis had reduced the D.P. to about 260, the degradation came to a standstill. On the other hand, for viscose rayon the hydrolysis continued rapidly until the D.P. was 60, and then also came to a comparative standstill. They explained their results on the hypothesis of periodic weak linkages in the cellulose chains. The weak, acid-sensitive bonds were exposed only in the amorphous portions of the fiber. In native cellulose, most of the crystalline domains extend over such a region that the limiting hydrocellulose has a D.P. of 260, while in the more disorganized rayon fiber essentially all of the weaker bonds are exposed to the hydrolyzing agent.

Davidson [2] has made similar studies, using, for the most part, 6 or 10N HCl or H_2SO_4 at 20°C. However, he has concluded that the change in the rate of the reaction and the contrast between the hydrolysis of cellulose in homogeneous and heterogeneous systems are explained solely by "differences in the accessibility of glycosidic linkages to the acid, resulting from the partly crystalline, partly amorphous nature of the fibers." Pacsu has pointed out [11] some difficulties which make it unlikely that this hypothesis is sufficient to explain these phenomena. First of all, the ratio of crystalline to amorphous regions would have to be very different from that calculated from physical measurements [8]. Secondly, the moisture absorption of the hydrocellulose, as determined by Davidson, cannot be explained with his concept. And, finally, similar degradation results are obtained in a homogeneous solution in 85% phosphoric acid where, Davidson says, the "crystalline regions are broken up and the acid acquires access to every linkage."

However, the crystalline nature of the fiber does impose certain limits on the hydrolysis, as demonstrated by the different limit hydrocelluloses obtained by Mehta and Pacsu from native cellulose and viscose rayon. Hermans has shown [7] that water can penetrate into the crystalline portions of mercerized and regenerated cellulose but cannot get into any but the amorphous part of native cellulose. This would indicate that all the hydrolyzable bonds in rayon are exposed to the action of aqueous reagents, whereas in cotton fibers some are protected. Thus, the D.P. of limit hydrocellulose from viscose should represent the distance along the glucose residue chains which separates acid-sensitive bonds.

In fibrous methyl cellulose, the extensiveness of the crystalline regions of the native fiber should be largely retained. However, the nature of the intermolecular forces between chains would no longer show the great difference that exists in those between chains in crystalline regions of native cellulose, where hydrogen bonding must be nearly complete, and in those in amorphous areas where hydrogen bridges are less regular. The substitution of methyl groups on the hydroxyls removes the possibility of hydrogen bonding and causes the intermolecular forces to be much more nearly alike throughout the fiber. There still exists, of course, a difference in these forces in crystalline and amorphous regions, but its reduced magnitude, together with the increased hydrophobic nature of the whole fiber, should minimize differences in accessibility to an aqueous reagent. A heterogeneous mild-acid hydrolysis should therefore be expected to be little influenced by crystallinity differences and, on the basis of Pacsu's hypothesis, should proceed straightforwardly to break essentially all of the acid-sensitive linkages, yielding a product the average D.P. of which is a measure of the average spacing of the weak acid-sensitive links along the glucose chain.

Preparation of Methyl Cellulose

Cellulose was considered by Payen, who described and named it in 1838, to be that part of the walls of plant cells derived exclusively from glucose and resembling cotton cellulose in its physical and chemical properties. In later decades, particularly from 1890 to 1920 when Cross and Bevan dominated the field of cellulose research, cellulose was believed by many investigators to be chemically bound to the varying incrusting materials found with it in most plants, so that the celluloses prepared from various sources were separate chemical entities. However, as the micellar structure became firmly established by birefringence, x-ray, and other studies, and as a deeper insight into the chemical nature of cellulose was gained, cellulose came to be considered the same material when derived from any source and properly

freed from mechanically mixed impurities, and the original concept of Payen was re-established.

In view of the drastic purification treatments involved in separating cellulose from many sources and the sensitive nature of some of the recently revealed fine structure, it is again a matter of some doubt whether cellulose derived from various plants is in all respects identical [14]. However, cotton cellulose, because of its fairly high natural purity, its role in the development of our knowledge of cellulose (which is no doubt due largely to its easy purification), and its economic importance, has been chosen by most investigators as a standard normal form of cellulose, and hence the methyl cellulose used in these experiments was prepared from the native cellulose of American cotton.

The cotton had been processed through the usual cotton opening, picking, and carding machinery, and was received in the form of sliver which was exceptionally free from foreign material such as bits of twigs, leaves, or seeds. Half-pound lots of the sliver were further purified by solvent extraction and a light alkali boil. It was first boiled for 10 hrs. in acetone, and then for 10 hrs. in benzene. After the first 3 hrs. of each treatment, the solvent which would readily drain from the material was poured off and replaced with fresh liquid at approximately half-hour intervals. After as much as possible of the benzene had been squeezed or centrifuged out, the cotton was allowed to dry in the air overnight, and was then boiled for 6 hrs. in 2% aqueous sodium hydroxide under a stream of oxygen-free nitrogen. It was washed in hot tap water, soured with dilute acetic acid, and kept 18 hrs. in running tap water. Finally, it was washed in 8 portions of hot distilled water and in 3 portions of methanol, and was dried in the air. In the final washings a basket centrifuge was used to remove each portion of wash liquor from the material.

The procedure for methylation was essentially that which was introduced by Haworth and his school [6] for the complete methylation of di- and oligosaccharides. It consists of treating the cellulose with very strong aqueous sodium hydroxide followed by dimethyl sulfate.

Cellulose in the presence of strong alkali is degraded by the oxygen of the air, especially at higher temperatures, and in order to avoid this deterioration as much as possible it has been suggested that the methylation be carried out under nitrogen [17] and at room temperature [18]. Although the latter decreases the rate of methylation considerably so that the alkali is in contact with the cellulose for a much longer period, the rate of degradation is apparently even more reduced, and if oxygen can be excluded fairly well, it would appear that the low-temperature procedure would be much safer than the 50° to 70° C used by Haworth.

When liquid dimethyl sulfate is added to cellulose wet with caustic solution, a vigorous exothermic reaction occurs shortly, undoubtedly being both the methylation and the hydrolytic side reaction of the dimethyl sulfate and alkali:

$$\begin{matrix} CH_3O \\ \\ CH_3O \end{matrix} \!\!> SO_2 + 2\,NaOH \rightarrow Na_2SO_4 + 2\,CH_3OH.$$

In order to achieve a low-temperature methylation, this vigorous reaction must be avoided. This is conveniently done by an expedient which also provides an effective means for shielding the reaction mixture from oxygen—that is, dilution of the dimethyl sulfate with a considerable volume of toluene. The use of a diluent has been proposed before, as early as the work of Denham and Woodhouse [3], who used benzene in some of their experiments.

The optimum concentration of sodium hydroxide favoring yield, efficient use of dimethyl sulfate, and retention of fiber structure is apparently 40% to 45% [9]. Since this is far above the concentration at which maximum swelling of the fiber occurs, it would appear that the degree of swelling is not a major factor.

The methylation reaction can be written as follows:

$$\begin{matrix} Cel{-}OH + \\ \\ NaOH + \\ \\ \\ \\ \\ \\ \end{matrix} \!\!> \begin{matrix} \\ CH_3O \\ \\ CH_3O \\ \\ NaO \\ \\ CH_3O \end{matrix} \!\!> \begin{matrix} \\ \\ \\ SO_2 \rightarrow \\ \\ \\ SO_2 + Cel{-}OCH_3 + H_2O, \\ \\ \end{matrix}$$

but a very large excess of both sodium hydroxide and dimethyl sulfate is necessary to obtain the maxi-

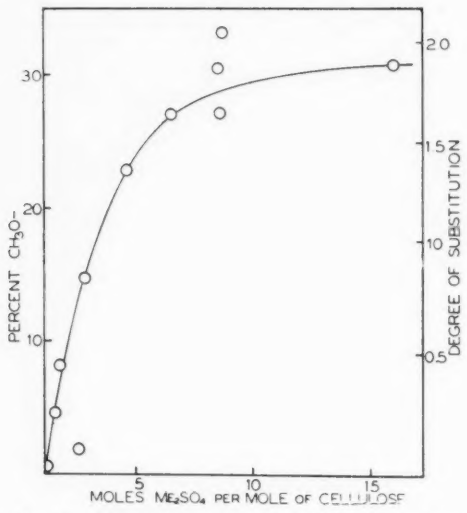


FIG. 1. *Methoxyl content reached by single-stage methylation of cellulose.*

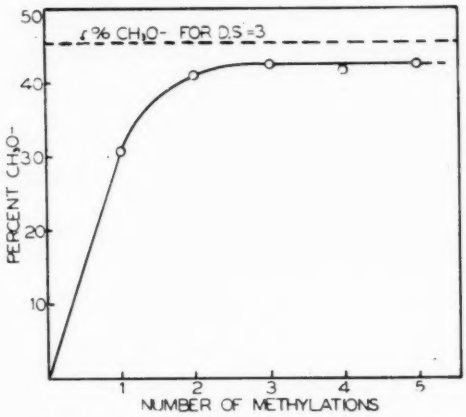


FIG. 2. *Methoxyl content reached by repeated methylation of cellulose.*

mum reaction. Table I and Figure 1 show the effect of the excess of dimethyl sulfate on the methoxyl content of the product. The sodium hydroxide was approximately constant in all the preparations.

With the above considerations in mind, the following procedure was chosen for methylation. Ten grams of purified native cellulose were steeped for 40 min. in 40% aqueous caustic soda (weight percent) at room temperature. As much as possible of the excess caustic solution was then removed by pressing on a Buchner funnel over a vacuum flask, centrifuging in a basket centrifuge, or simply squeezing by hand using neoprene gloves. The amount of solution remaining in the cotton was 3 to 3.5 times the weight of the cotton. The damp material was then suspended in 500 ml. of toluene in a glass-stoppered bottle and 50 ml. (66.7 g.) of dimethyl sulfate were added. The mixture was shaken thoroughly and allowed to stand overnight. Continuous, vigorous shaking was used in the early preparations, but this was later found to be of no value in increasing the degree of methylation.

After removing the excess toluene on a suction funnel or in a centrifuge, the material was washed with boiling distilled water until free of toluene and sodium hydroxide. The best means of removing the toluene was to place the beaker containing the product covered with boiling water into a boiling-water bath and to stir continuously for 10 or 15 min. Several such washes served to remove the toluene very effectively. In order to retain the maximum fiber structure it is essential that the wash water be near the boiling point when added to the material. When the methylated cellulose had been thoroughly washed, it was dewatered as much as possible on a Buchner funnel and then dried in an oven at 55°C.

The product resulting from such a one-step procedure was a white, fibrous material containing 27% to 31% methoxyl instead of the theoretical 45.6%. It was insoluble in organic solvents, but soluble in cold water and cold aqueous caustic-soda solutions.

In order to obtain a more completely methylated material, the above procedure must be repeated. If the dry product of the first methylation is used, it must be soaked in water and centrifuged before it

TABLE I. EFFECT OF DIMETHYL SULFATE CONCENTRATION ON THE METHYLATION OF CELLULOSE

Sample No.	Moles Me_2SO_4 per mole of cellulose	Percent CH_3O— in product
X-93-a	17.1	30.7
X-95	8.6	33.7
X-72	8.5	27.1
X-66	8.4	30.5
X-58	6.1	27.0
X-62	4.0	22.9
X-63	2.0	14.6
X-64	1.7	1.9
X-72-c	0.8	8.1
X-72-b	0.4	4.5
X-72-d	0.09	0.5

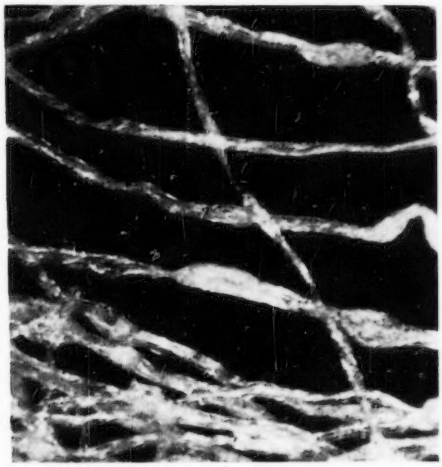


FIG. 3. *Photomicrograph of methylated cotton fibers. (Magnification 120 ×.)*

will be wet and swollen by the sodium hydroxide solution. However, the over-all yield is much improved if the material is not washed and dried after the first methylation, but is re-treated until the degree of substitution has become so high that the material is no longer water-soluble. This can be done by taking the material before washing, freeing it as much as possible of toluene and spent caustic solution, and steeping it immediately in fresh 40% caustic. Two fresh portions of caustic were used, the material remaining in each for approximately 20 min. It was then squeezed or centrifuged, suspended again in toluene, and dimethyl sulfate was added as before. After two such remethylations, the material was insoluble in water, and could be washed with much less loss.

The number of steps required to reach a maximum methoxyl content is shown in Figure 2 and by the following data:

Number of methylations	Percent CH_3O—
1	30.72
2	41.06
3	42.46
4	41.87
5	42.78

In the experiment from which these data were obtained, the product was washed after each step, and, as can be seen, the methylation was essentially complete after three steps. When the material is not washed but is subjected to further methylation as suggested in the preceding paragraph, two steps usually suffice, each consisting of three treatments with caustic soda and dimethyl sulfate.

The product of repeated methylation, containing from 42.5% to 43.5% methoxyl, is still a white, fibrous substance. The photomicrograph in Figure 3 shows how similar in form the methylated fibers are to the native cellulose fiber. The twisted ribbon

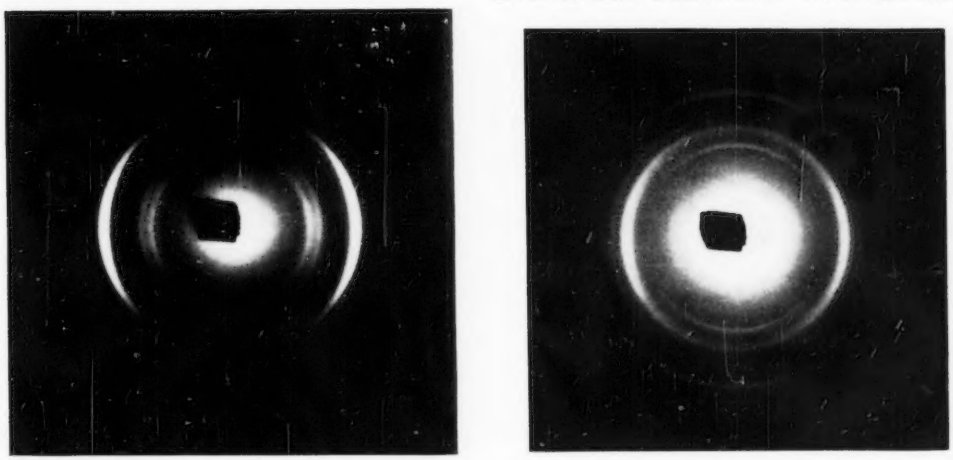


FIG. 4. *X-ray diffraction fiber diagrams of native cellulose* (left) *and trimethyl cellulose* (right).

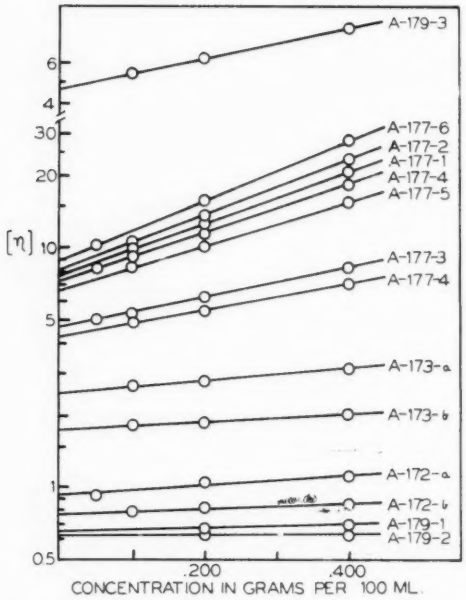


FIG. 5. *Determination of intrinsic viscosity of methyl cellulose in chloroform.*

form of the cotton fiber is still apparent. The fibers are readily soluble in chloroform, and somewhat less so in pyridine. They are insoluble in oxygenated solvents such as alcohols, ethers, and ketones, and in such chlorinated solvents as carbon tetrachloride and trichloroethylene. The degree of polymerization determined by viscosity measurements in chloroform solution was 700 to 900. Figure 4 shows the x-ray diffraction fiber diagram of the product compared with that of native cellulose and indicates that the crystalline nature of the original fiber is largely retained.

Methoxyl analyses were done according to the procedure first proposed by Viebock and Schwappach [19] and later modified by Clark [1]. Samples of 10 to 20 mg., weighed to within ± 0.02 mg., were used, depending upon the expected methoxyl content. For nearly completely methylated cellulose, a sample of 10 mg. required approximately 8 ml. of 0.1*N* thiosulfate, which was a convenient amount to measure in a microburet. The samples were dried in a vacuum desiccator charged with fresh phosphorus pentoxide before their final weights were determined. The samples were first weighed roughly

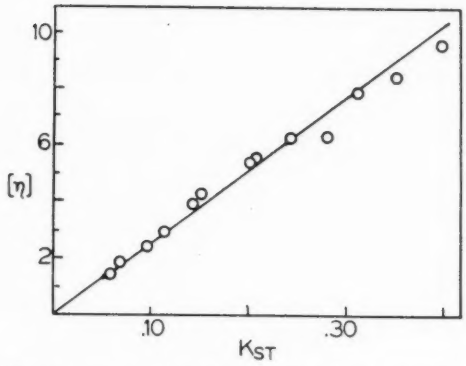


FIG. 6. *Relationship between intrinsic viscosity and slope of the* $\frac{\eta_{sp}}{c}$ *vs. c curve.*

into tared tin or aluminum foil cups and placed in the desiccator. After 18 hrs., air was slowly admitted through a magnesium perchlorate drying tube. The top of the desiccator was removed and the foil cups were quickly closed with a pair of tweezers. In this manner the final weighing could be made unhurriedly without absorption of moisture by the material.

Several slight changes were made in the procedure as given in the references above. A stream of dry, oxygen-free nitrogen was frequently used instead of carbon dioxide as the entraining gas for carrying the liberated methyl iodide over into the receiver. Both were equally satisfactory.

It was found desirable to use 10 ml. instead of 5 ml. of 25% sodium-acetate solution in the flask into which the contents of the receiver were washed. Using only 5 ml. frequently resulted in solutions which could not be completely decolorized by the

TABLE II. HETEROGENEOUS HYDROLYSIS OF METHYL CELLULOSE (42.34% CH_3O—, 60°C, 1*N* HCl)

Sample No.	Time (hrs.)	[η]	D.P. $K_m = 11 \times 10^{-4}$
A-167-a	0	9.90	900
A-168-a-1	0.5	8.60	782
A-168-a-2	1.0	8.10	736
A-168-a-3	2.0	6.60	600
A-168-a-4	4.3	5.60	509
A-168-a-5	8.0	4.15	377
A-168-a-6	16.0	3.17	288
A-173-a	27.8	2.50	227
A-173-b	49.7	1.76	160
A-179-3	270.2	0.66	60
A-179-4	366.3	0.64	58

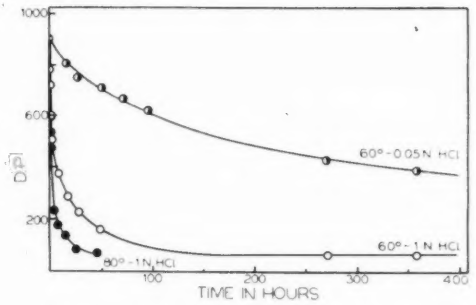


FIG. 7. *Heterogeneous hydrolysis of trimethyl cellulose.*

formic acid, thus ruining the determination. This happened usually with the first sample run in a fresh charge of phenol and hydriodic acid. Although the use of more of the neutralizing solution apparently corrected this difficulty, as a further precaution the phenol-acid mixture was gently boiled for 15 min. with the gas stream on before the first sample and receiver were added. This also avoided the larger than usual blank associated with the first sample run on a fresh charge. Not more than 4 samples were run in each charge.

The molecular weights of trimethyl cellulose preparations were measured by Staudinger's viscosimetric technique, using chloroform solutions in an Ostwald-Cannon-Fenske pipet. The constant, K_m, was found to be 11×10^{-4} by Staudinger and Reinecke [16], who determined the K_m osmometrically for a series of ether-acetates and extrapolated to the tri-ether. The range of D.P. in which K_m was determined was 200 to 450.

The Staudinger equation was used in the form

$$\frac{[\eta]}{10} = \text{D.P.} \times K_m,$$

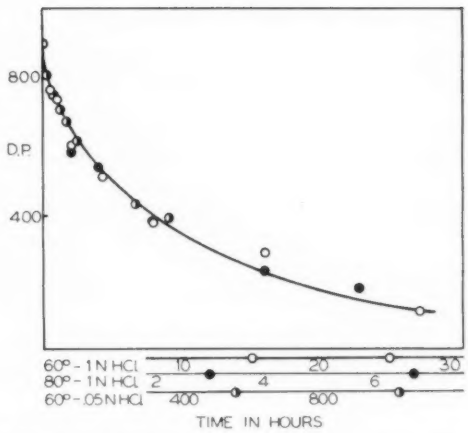


FIG. 8. *Data from Figure 7 replotted with adjusted time scales.*

where

$$[\eta] = \frac{\lim_{c=0} \eta_{sp}}{c} = \frac{\lim_{c=0} \eta_{rel} - 1}{c},$$

and the concentration, c, is expressed in grams of trimethyl glucose anhydride units per 100 ml. of solution.

Kinetic-energy corrections were made on all the data using the method of Wagner [20].

Hydrolysis

Hydrolysis experiments were performed in the following way: 200-mg. samples of trimethyl cellulose were weighed out into 175×22-mm. test tubes. A single sample of the same weight was weighed out with each group of hydrolysis samples for an oven moisture determination, which usually showed about 1.5% moisture in the material. The hydrolysis samples were covered with 20 ml. of acid

TABLE III. HETEROGENEOUS HYDROLYSIS OF METHYL CELLULOSE
(42.34% CH_3O—, 80°C, 1 *N* HCl)

Sample No.	Time (hrs.)	$[\eta]$	D.P., $K_m = 11 \times 10^{-4}$
A-170-a-1	0.5	6.50	591
A-170-a-2	1.0	5.90	536
A-170-a-3	2.0	4.17	379
A-170-a-4	4.0	2.60	236
A-170-a-5	7.5	2.08	189
A-170-a-6	16.0	1.52	138
A-172-a	24.0	0.94	85
A-172-b	46.9	0.77	70

TABLE IV. HETEROGENEOUS HYDROLYSIS OF METHYL CELLULOSE
(42.34% CH_3O—, 60°C, 0.05 *N* HCl)

Sample No.	Time (hrs.)	$[\eta]$	D.P., $K_m = 11 \times 10^{-4}$
A-177-6	15.8	8.9	809
A-177-2	26.7	8.2	745
A-177-1	50.3	7.75	705
A-177-4	72.0	7.3	664
A-177-5	96.0	6.7	609
A-179-1	270.3	4.7	427
A-179-2	366.3	4.28	389

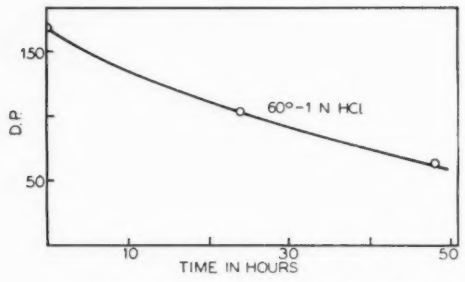


FIG. 9. *Heterogeneous hydrolysis of trimethyl hydrocellulose.*

of the desired strength, and entered in a water bath maintained at the desired temperature ±0.5° C. When the acid had reached the temperature of the bath, the tubes were tightly corked. At the end of the hydrolysis period, the samples were filtered from the acid onto tared sintered-glass crucibles, washed, and weighed to constant weight. Methoxyl analyses and molecular weight determinations were then made.

The value of $[\eta]$ for each sample was obtained by determining η_{sp}/c at several concentrations and extrapolating a semilogarithmic plot to zero concentration, as shown by the curves in Figure 5. The slope of such curves has a value which is characteristic for a given high-polymeric substance in a given solvent, and is also directly proportional to the limiting intrinsic viscosity, as shown by Figure 6. This slope has been designated as the "Steigungskonstante," K_{St}, by Staudinger and Heuer [15]. With it the limiting intrinsic viscosity, and consequently the D.P., may be determined from a single determination of the intrinsic viscosity at a suitable concentration by using the following formula:

$$\log [\eta] = \log \frac{\eta_{sp}}{c} - K_{St} \cdot c.$$

K_{St} is valid only for a given concentration of a given polymer-solvent system. Since it varies directly with $\log [\eta]$, as shown in Figure 6, it may be replaced by $K' \log [\eta]$ so that the above equation becomes

$$\log [\eta] = \frac{\log (\eta_{sp}/c)}{1 + K'c},$$

where K' depends on the polymer-solvent system but not on the concentration. However, all the data given below were obtained by making several determinations and extrapolating.

The results of a series of hydrolysis experiments are summarized in Tables II, III, and IV, and in Figure 7.

In the first stages of the hydrolysis there is a rapid drop in the degree of polymerization, which shortly is reduced to a point where further attack is comparatively slow. The D.P. at this point is approximately 60.

Figure 8 shows the data from the early part of the curves in Figure 7 replotted with a triple-abscissa scale. With this adjustment of the time scale, the three curves become very much the same, indicating a similar course of reaction in each case.

The results of a similar hydrolysis experiment on a sample of trimethyl cellulose which had been prepared from the limit hydrocellulose of native cotton are shown in Figure 9 and Table V.

Fifteen grams of purified cotton were hydrolyzed with 450 ml. of 1*N* HCl for 24 hrs. at 60° C, then methylated in four steps to a methoxyl content of 43.01%. Upon hydrolysis of the methylated material, the D.P. does not show the sudden and rapid drop characteristic of the hydrolysis of native cellulose and the methyl cellulose prepared from it. Instead, it is reduced at a moderate rate toward the limiting value obtained in the hydrolysis of the higher-molecular-weight material.

If the structure for cellulose proposed by Pacsu is correct, these results would indicate that in this reaction all of the acid-sensitive linkages are available to the reagent and that the distance between the weaker bonds is of the order of 60 residues. The behavior of trimethyl cellulose and trimethyl hydrocellulose corresponds very closely to that observed in the mild hydrolysis of cellulose, regenerated cellulose, and hydrocellulose. The shapes of the D.P. *vs.* time curves for trimethyl cellulose and trimethyl hydrocellulose are very similar to those for the respective unmethylated materials, while the limiting

TABLE V. HETEROGENEOUS HYDROLYSIS OF METHYL HYDROCELLULOSE (60° C, 1*N* HCl)

Sample No.	Time (hrs.)	$[\eta]$	D.P. $K_m = 11 \times 10^4$
A-100-a	0.0	1.85	168
A-135-a	24.0	1.14	104
A-135-b	48.0	0.74	68

TABLE VI. WEIGHT LOSS DURING HYDROLYSIS OF METHYL CELLULOSE

Sample No.	Conditions of hydrolysis		Time (hrs.)	Weight loss (%)
A-167-a	60°C	1.N HCl	0.0	0.0
A-168-a-1	60°C	1.N HCl	0.5	0.6
A-168-a-2	60°C	1.N HCl	1.0	0.4
A-168-a-3	60°C	1.N HCl	2.0	0.1
A-168-a-4	60°C	1.N HCl	4.3	0.3
A-168-a-5	60°C	1.N HCl	8.0	0.2
A-168-a-6	60°C	1.N HCl	16.0	0.5
A-173-a	60°C	1.N HCl	27.8	0.0
A-173-b	60°C	1.N HCl	49.7	0.0
A-179-3	60°C	1.N HCl	270.2	5.9
A-179-4	60°C	1.N HCl	366.3	7.8
A-170-a-1	80°C	1.N HCl	0.5	0.0
A-170-a-2	80°C	1.N HCl	1.0	0.15
A-170-a-3	80°C	1.N HCl	2.0	0.15
A-170-a-4	80°C	1.N HCl	4.0	0.5
A-170-a-5	80°C	1.N HCl	7.5	0.75
A-170-a-6	80°C	1.N HCl	16.0	1.6
A-172-a	80°C	1.N HCl	24.0	2.35
A-172-b	80°C	1.N HCl	46.9	4.8
A-177-6	60°C	0.05N HCl	15.8	0.0
A-177-2	60°C	0.05N HCl	26.7	0.0
A-177-1	60°C	0.05N HCl	50.3	0.0
A-177-4	60°C	0.05N HCl	72.0	0.0
A-177-5	60°C	0.05N HCl	96.0	0.0
A-179-1	60°C	0.05N HCl	277.3	
A-179-2	60°C	0.05N HCl	366.3	0.45

value in each curve is close to that for regenerated cellulose.

If the limiting D.P. attained in such heterogeneous hydrolysis experiments is to be attributed to the occurrence of non-accessible crystalline regions where chains of this length are protected from the action of the reagent, then the limiting D.P. should be a measure of the extent of the crystalline portions of the fiber. This would indicate that trimethylcellulose had considerably smaller crystalline regions than the native cellulose from which it was prepared, because its limiting D.P. is 60 instead of 260. However, there is no reason to expect that methylation would disorganize the fiber to this extent, especially in view of the fact that methylation of hydrocellulose, the short chains of which should be much more susceptible to such disorganization, gives a product with the same limiting D.P. as native cellulose.

In the experiments described in Tables II, III, and IV there is a small loss in weight during the hydrolysis which varies with the conditions. Its extent, shown by the data of Table VI, is not considered to be sufficient to change the results or interpretation. It must be attributed to the slow hydrolysis of 1,4-glycosidic bonds to produce chains short enough to dissolve.

There was no appreciable change in the methoxyl content during the reaction.

Calculation of Apparent Rate Constant

The following assumptions were made to calculate an apparent rate constant for the hydrolysis reaction: (1) all hydrolyzable bonds are accessible to the reagent, and (2) the reaction follows first-order reaction kinetics. Then, let

$\overline{\text{D.P.}}_t$ = average degree of polymerization at time t,
n = number of molecules at time t,
$\overline{\text{D.P.}}_0$ = average degree of polymerization at zero time,
n_0 = original number of molecules.

The number of bonds broken in time t will be equal to the increase in the number of molecules at that time, since each bond split adds one to the number of molecules. Then

$$\text{Number of bonds broken} = \Delta n = n - n_0. \quad (1)$$

However, the number of molecules at a given time is equal to the total number of glucose residues present divided by the $\overline{\text{D.P.}}_t$ for that time. The total number of glucose residues is given by $n_0(\overline{\text{D.P.}}_0)$, so that

$$\Delta n = \frac{n_0(\overline{\text{D.P.}}_0)}{\overline{\text{D.P.}}_t} - n_0$$

$$= \frac{n_0(\overline{\text{D.P.}}_0 - \overline{\text{D.P.}}_t)}{\overline{\text{D.P.}}_t}. \quad (2)$$

From first-order reaction kinetics:

$$k = \frac{1}{t} \ln \frac{c_0}{c_t},$$

where c_0 and c_t are the concentrations of bonds at zero time and at time t, respectively. However, as stated above, the change in the number of bonds is equal to the change in the number of molecules, so that

$$k = \frac{1}{t} \ln \frac{c_0}{c_0 - \Delta n}. \quad (3)$$

Since each molecule has D.P. − 1 bonds in it, the original number of bonds, c_0, will be equal to

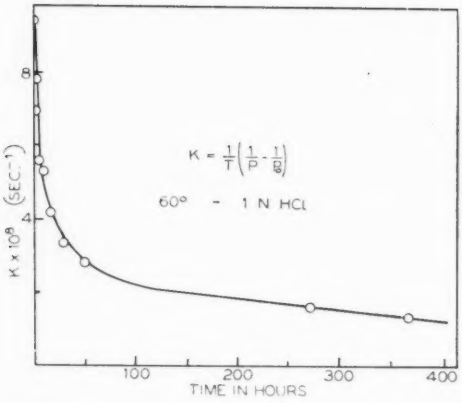


FIG. 10. *Change in apparent rate constant during heterogeneous hydrolysis of trimethyl cellulose.*

$n_0(\text{D.P.}_0 - 1)$. By using this and equation (2), equation (3) becomes

$$k = \frac{1}{t} \ln \frac{n_0(\text{D.P.}_0 - 1)}{n_0(\text{D.P.}_0 - 1) - n_0\left(\frac{\text{D.P.}_0 - \text{D.P.}_t}{\text{D.P.}_t}\right)}$$

or

$$k = \frac{1}{t} \ln \frac{\text{D.P.}_t(\text{D.P.}_0 - 1)}{\text{D.P.}_0(\text{D.P.}_t - 1)}. \qquad (4)$$

As an endless series, equation (4) can be written

$$k = \frac{1}{t}\left(\frac{\text{D.P.}_0 - \text{D.P.}_t}{\text{D.P.}_0\text{D.P.}_t}\right) + \frac{1}{2t}\left(\frac{\text{D.P.}_0^2 - \text{D.P.}_t^2}{\text{D.P.}_0^2\text{D.P.}_t^2}\right) + \frac{1}{3t}\left(\frac{\text{D.P.}_0^3 - \text{D.P.}_t^3}{\text{D.P.}_0^3\text{D.P.}_t^3}\right) + \cdots$$

TABLE VII. RATE CONSTANT FOR HYDROLYSIS OF METHYL CELLULOSE (60° C, 1 N HCl)

Time (hrs.)	D.P.	$k \times 10^5$ (sec.$^{-1}$)
0.0	900	
0.5	782	9.4
1.0	736	6.9
2.0	600	7.8
4.3	509	5.6
8.0	377	5.3
16.0	288	4.2
27.8	227	3.3
19.7	160	2.8
270.2	60	1.6
366.3	58	1.2

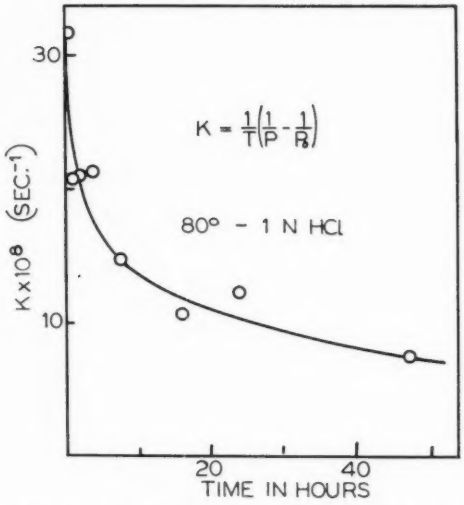


FIG. 11. *Change in apparent rate constant during heterogeneous hydrolysis of trimethyl cellulose.*

For reasonably large values of D.P._0 and D.P._t, only the first term need be considered and it reduces to

$$k = \frac{1}{t}\left(\frac{1}{\text{D.P.}_t} - \frac{1}{\text{D.P.}_0}\right). \qquad (5)$$

This equation has been derived in a different way by af Ekenstam [5], who used it to study the hydrolysis of cellulose in acid solution. His equation corresponding to equation (4) can be written as

$$k = \frac{1}{t} \ln \frac{M_t(M - m)}{M(M_t - m)}, \qquad (6)$$

where M_t = average molecular weight at time t, M = average molecular weight at beginning, and

TABLE VIII. RATE CONSTANT FOR HYDROLYSIS OF METHYL CELLULOSE (80° C, 1 N HCl)

Time (hrs.)	D.P.	$k \times 10^5$ (sec.$^{-1}$)
0.0	900	
0.5	591	32.2
1.0	536	21.1
2.0	379	21.4
4.0	236	21.7
7.5	189	15.0
16.0	138	10.8
24.0	85	12.5
46.9	70	7.8

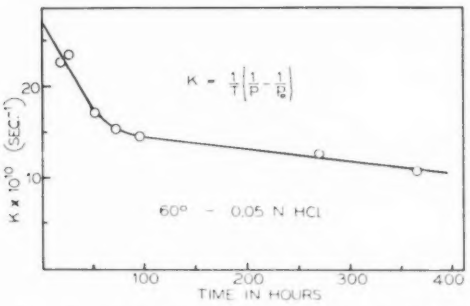


FIG. 12. *Change in apparent rate constant during heterogeneous hydrolysis of trimethyl cellulose.*

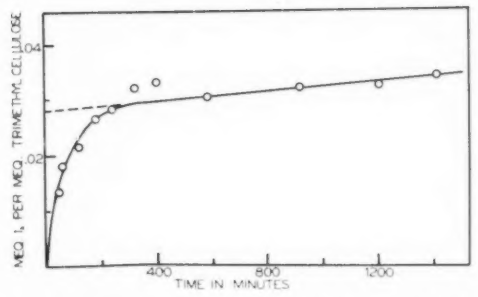


FIG. 13. *Alkaline hypoiodite oxidation of hydrolyzed trimethyl cellulose.*

m = average molecular weight at end. Af Ekenstam has shown that this equation is equivalent to that used by Freudenberg and Kuhn in the "kinetic proof."

The rate constants calculated from equation (4) or (5), which give the same result, for the hydrolysis experiments in the previous subsection are given in Tables VII, VIII, and IX, and are shown graphically in Figures 10, 11, and 12.

The rapid initial change in the rate constant, followed by a comparative leveling out, is typical of the previous results of similar experiments by Mehta and Paesu using organic acids on cotton, by af Ekenstam with cotton in H_3PO_4 solution, and by Steurer, who exposed methyl-cellulose solutions to ultraviolet irradiation. This appears to be further evidence that two different reactions are occurring in the degradation process.

End-Group Determination

The determination of D.P. by viscosity measurements may be affected by differences between the dispersity of the sample measured and that of the material with which the constant K_m was determined, by the fact that the constant may not be valid over a larger range of D.P. than that used in its determination, and by uncertainties concerning the validity of the viscosity law itself. For such reasons it was desirable to check the D.P. of the limit hydrocellulose obtained in the above experiments by some other method. This was done by measuring the oxidation of the hydrocellulose in buffered alkaline hypoiodite solution according to the method of Martin, Smith, Whistler, and Harris [10].

Only one modification of the procedure was made, which was necessary because part of the iodine was so strongly adsorbed on the methyl cellulose that the end point could not be determined satisfactorily. The addition of 50 ml. of chloroform to the acidified suspension, just before titration, corrected this difficulty by dissolving the methyl cellulose and freeing the iodine. With this change the end point could be determined quite satisfactorily.

A sample of limit hydro-trimethyl cellulose was prepared by hydrolyzing 27 g. of trimethyl cellulose

TABLE IX. RATE CONSTANT FOR HYDROLYSIS OF METHYL CELLULOSE (60° C, 0.05 *N* HCl)

Time (hrs.)	D.P.	$k \times 10^{10}$ (sec.$^{-1}$)
0.0	900	
15.8	809	22.8
26.7	745	23.6
50.3	705	17.2
72.0	664	15.6
96.0	609	14.7
270.3	427	12.8
366.3	389	10.8

TABLE X. OXIDATION OF HYDRO-TRIMETHYL CELLULOSE BY ALKALINE HYPOIODITE (pH 10.6, 0° C, 42.87% CH_3O —)

Time (min.)	Meq. I_2 consumed per g. sample	Meq. I_2 consumed per meq. trimethyl glucose residues
30	0.068	0.0136
60	0.091	0.0182
120	0.108	0.0216
180	0.134	0.0268
240	0.146	0.0292
322	0.163	0.0326
400	0.167	0.0334
583	0.153	0.0306
920	0.162	0.0324
1205	0.165	0.0330
1419	0.174	0.0348

(P-21-a) with 1,000 ml. of 1*N* HCl for 164 hrs. at 60° C. The yield was 25.75 g. (95%) of material the D.P. of which (determined by viscosity measurements) was 80. The consumption of iodine at 0°C in sodium carbonate-bicarbonate buffer at pH 10.6 is shown by the data in Table X and Figure 13.

Unexpectedly, even trimethyl cellulose appears to be subject to overoxidation in this medium, but its rate is slow compared to the initial consumption. Extrapolation of the flatter portion of the curve to zero time indicates that the material consumes 0.028 milliequivalent of iodine for each milliequivalent of trimethyl glucose residues. Two moles of iodine are necessary to oxidize each mole of end-group; therefore, this quantity of iodine is equivalent to a D.P. of 71. This is approximately 11% lower than the viscosimetric figure, but indicates that viscosity measurements may be used with about this degree of reliability in this range. The difference is in the direction expected when comparing number-average and "viscosity-average" molecular weights, but it is so small that it indicates a fair degree of uniformity in the material.

Hydrolysis of Methyl Cellulose of a Lower Degree of Substitution

The product of one-step methylation contains 27–30% CH_3O—, which means that about 2 out of every 3 hydroxyl groups on each glucose residue have been substituted. It was hoped that the resulting disorganization of the chain molecules would be so great that heterogeneous hydrolysis would not be affected by crystallinity differences. However, the inhomogeneity of such a material with respect to the degree of substitution of various chains makes the material useless for such experiments. The behavior of a partially methylated cellulose when hydrolyzed with 2*N* sulfuric acid at 70° C is shown by Table XI and Figure 14.

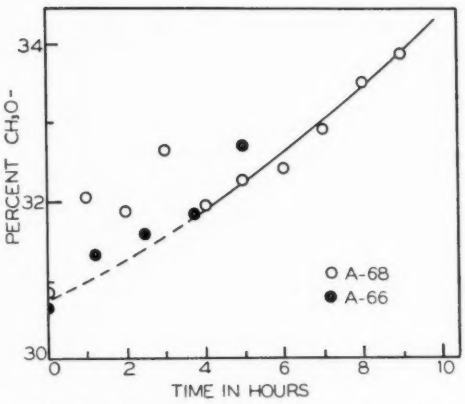


FIG. 14. *Heterogeneous hydrolysis of partially methylated cellulose.*

This behavior is undoubtedly connected with the inhomogeneous substitution of the cellulose due to the topochemical nature of the etherification, and is apparently caused by the preferential solubility of low methoxyl-content methyl cellulose in the dilute acid. The loss in weight of the hydrolyzed samples was found to be rather large, and was considerably larger than the loss in distilled water under the same conditions. The latter shows that the hydrolytic action of the acid was probably also in-

TABLE XI. HYDROLYSIS OF PARTIALLY METHYLATED CELLULOSE
(30.86% CH_3O—, 70° C, 2*N* H_2SO_4)

Sample No.	Time (hrs.)	Percent CH_3O
A-68	0	30.86
A-68-1	1	32.06
A-68-2	2	31.89
A-68-3	3	32.65
A-68-4	4	31.96
A-68-5	5	32.29
A-68-6	6	32.42
A-68-7	7	32.91
A-68-8	8	33.53
A-68-9	9	33.89
A-66-1	0	30.66
A-66-6	1.25	31.33
A-66-5	2.50	31.60
A-66-4	3.75	31.85
A-66-2	5.00	32.71

TABLE XII. WEIGHT LOSS IN THE HYDROLYSIS OF PARTIALLY METHYLATED CELLULOSE
(10 hrs., 70°C)

Sample No.	Conc. of acid	Weight loss (%)	Percent CH_3O— Original	Final
A-70-1	2*N* H_2SO_4	34.8	30.72	33.13
A-70-2	2*N* H_2SO_4	31.3	30.72	—
A-70-3	Dist. H_2O	3.8	30.72	30.60
A-70-4	Dist. H_2O	13.5	30.72	30.23
A-72-1	2*N* H_2SO_4	15.33	27.14	28.41
A-72-2	2*N* H_2SO_4	15.28	27.14	28.33
A-72-3	Dist. H_2O	0.87	27.14	27.21
A-72-4	Dist. H_2O	0.50	27.14	27.51

volved. Results of experiments showing the magnitude of these weight losses are shown in Table XII.

Because this hydrolysis was complicated by these factors, no further study was made to determine the change in D.P. during such an experiment.

Conclusions

1. The heterogeneous, mild-acid hydrolysis of trimethyl cellulose slows down markedly when a D.P. of about 60 is reached. This is interpreted as indicating that the distance between acetal cross-bonds in the periodic structure proposed by Pacsu is this number of glucose residues.

2. The heterogeneous, mild-acid degradation of partially methylated cellulose confirms the heterogeneity of this material and the topochemical nature of the methylation reaction.

Summary

The preparation of trimethyl cellulose and its hydrolysis with 1*N* HCl at 60° and 80° C. and with 0.05*N* HCl at 60° C were studied. The course of the hydrolysis is similar in each case and a limiting D.P. of 60 is indicated. This is interpreted to indicate that the distance between acetal linkages in the periodic structure proposed for cellulose is this number of glucose residues. An equation for an apparent rate constant is derived, assuming first-order reaction kinetics. The apparent rate constant changes rapidly at first, but more and more slowly as the D.P. falls from 900 to 60. The order of magnitude of the limiting D.P. value, which has been determined viscosimetrically, was confirmed by hypoiodite titration.

Partially methylated cellulose (30% CH_3O—) was hydrolyzed with 2*N* H_2SO_4 at 70°C. The results confirm the topochemical nature of the methylation reaction.

Literature Cited

1. Clark, E. P., *J. Assoc. Offic. Agr. Chemists* **15**, 136 (1932).
2. Davidson, G. F., *J. Text. Inst.* **34**, T87 (1943).
3. Denham, W. S., and Woodhouse, H., *J. Chem. Soc.* **103**, 1755 (1913); **105**, 2357 (1914); **111**, 244 (1917).
4. Eisenhut, O., and Schwartz, E., *Angew. Chem.* **55**, 380 (1942).
5. Ekenstam, A. af, *Ber.* **69**, 549, 553 (1936).
6. Haworth, W. N., *J. Chem. Soc.* **107**, 8 (1915).
7. Hermans, P. H., "Contributions to the Physics of Cellulose Fibers," Amsterdam, Elsevier, 1946, pp. 41–8.
8. Hermans, P. H., *J. chim. phys.* **44**, 135 (1947).
9. Hess, K., Abel, G., Schön, W., and Komarewsky, V. I., *Cellulosechemie* **16**, 69 (1935); Atsuki, K., and Kagawa, I., *J. Soc. Chem. Ind. Japan* **37** (Supplemental Binding), 128 (1934); Ball, R. H., and Hibbert, H., *Can. J. Research* **7**, 481 (1932).
10. Martin, A. R., Smith, L., Whistler, R. L., and Harris, M., *J. Research Natl. Bur. Standards* **27**, 449 (1941).
11. Mehta, P. C., and Pacsu, E., TEXTILE RESEARCH JOURNAL **18**, 387 (1948).
12. Schulz, G. V., and Husemann, E., *Z. physik. Chem.* **B52**, 23 (1942); Husemann, E., and Schulz, G. V., *Z. physik. Chem.* **B52**, 1 (1942); Schulz, G. V., *Z. physik. Chem.* **B52**, 50 (1942); Husemann, E., *Makromol. Chem.* **1**, 140 (1947).
13. Simonsen, E., *Z. angew. Chem.* **10**, 219 (1898); Ost, H., and Wilkening, L., *Chem.-Ztg.* **34**, 461 (1910); Sherrard, E. C., and Gauger, W. H., *Ind. Eng. Chem.* **15**, 63 (1923).
14. Staudinger, H., "Makromolekulare Chemie und Biologie," Basel, Wepf & Co., 1947, p. 57; Staudinger, H., Herrbach, P., and Stock, H., *Makromol. Chem.* **1**, 60 (1947).
15. Staudinger, H., and Heuer, W., *Z. physik. Chem.* **A171**, 129 (1934).
16. Staudinger, H., and Reinecke, F., *Ann.* **535**, 47 (1938).
17. Staudinger, H., and Scholz, H., *Ber.* **67**, 84 (1934); Haworth, W. N., Montonna, R. E., and Peat, S., *J. Chem. Soc.* **1939**, 1899 (1939).
18. Urban, H., *Cellulosechemie* **7**, 76 (1926).
19. Viebock, F., and Schwappach, A., *Ber.* **63B**, 2818 (1930).
20. Wagner, R. H., *Anal. Chem.* **20**, 155 (1948).

(Manuscript received August 26, 1949.)

Cellulose Studies

XIV. The Fractionation and Solubility of Trimethyl Cellulose

Richard Steele and Eugene Pacsu

Contribution from the Textile Foundation and Frick Chemical Laboratory, Princeton University

IF THE PERIODIC, macromolecular structure for cellulose, postulating that it contains regularly spaced acid-sensitive linkages, is accepted, then the chain-length distribution in mildly hydrolyzed material should show high uniformity. Husemann and Schulz [3] have carefully fractionated the nitrated products of mild hydrolysis experiments and have found the expected degree of uniformity, centering around D.P. 500. Considering the more detailed chemical and morphological structure proposed by Pacsu, this result appears reasonable under the conditions which they used, but it also appears that their mild treatment did not break all of the weaker linkages. In order to verify this conclusion it would be necessary to fractionate materials corresponding to limit hydrocelluloses prepared from native cellulose and from regenerated cellulose. The first of these materials was fractionated by Mehta and Pacsu [2], and the expected sharpness of the distribution was found.

Upon hydrolysis, trimethyl cellulose is apparently degraded to a point which corresponds to the limit hydrocellulose prepared from regenerated cellulose, as shown above, and it was hoped that a fractionation of this material would complete the demonstration. The fractionation described below was done on a sample of the unhydrolyzed material so that its distribution curve would be available for comparison with that of the hydro-methyl cellulose. It is described in detail for two reasons: to make clear the difficulties involved and to justify the conclusion that methyl cellulose is not a desirable derivative for the intended experiment; and to provide a basis for a discussion of the solubility characteristics of trimethyl cellulose.

Fractionation

The scheme of the fractionation is shown by the diagram in Figure 1; the fractions obtained are summarized across the lower part of the figure.

Step 1

A 1% chloroform solution of 3.86 g. of trimethyl cellulose was prepared by shaking the material with one-half of the necessary solvent overnight, then using the remaining solvent to transfer the solution to a 3-liter flask. During the transfer the solution was filtered and 97 mg. of chloroform-insoluble material (B-39-d) were collected.

A commercial grade of petroleum ether, b.p. 60°–70° C, was used as a precipitant. The material was fairly pure hexane, its distillation curve showing only about 9% of high and low fractions boiling at more than 1° C from the boiling point of hexane. Over a period of 6 days the hexane was added to the solution in portions of about 200 ml. per day. The solution was kept in a constant-temperature room at 21.1° C (70° F), and the hexane was added very slowly with strong agitation of the flask. By the sixth day, 1,185 ml. of hexane had been added, but only a small sediment was present. This amounted to about 10 mg., and appeared to be more of the swollen but undissolved material which had escaped removal in the first filtration through glass wool. Upon the addition of 200 ml. of hexane on the sixth day, the solution became faintly milky in appearance. After standing overnight the turbidity increased only slightly, but it was possible by centrifugation to remove a small fraction (B-40-a), which was washed with hexane and dried.

The solution was now perfectly clear and hexane was added slowly until a faint turbidity again appeared. This required 380 ml. After standing overnight, the solution had precipitated a layer of thick gel on the bottom of the flask. This was collected by decantation, washed, and dried (B-40-b), and was found to comprise more than three-fourths of the sample. Addition of 300 ml. of hexane produced a further turbidity which yielded another fraction the next day (B-40-c). The solution was then

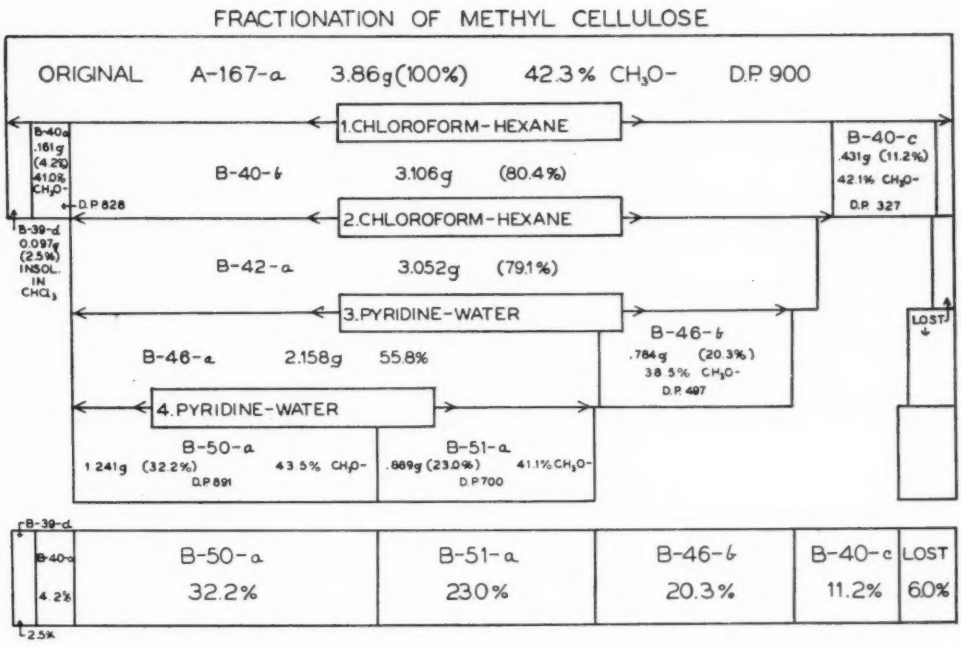


FIG. 1. *Summary diagram of steps used in the fractionation of trimethyl cellulose.*

evaporated and found to contain only a small amount (less than 10 mg.) of a syrupy material.

These operations had split off a head and a tail fraction. However, it was apparent that the usual criterion for judging the amount of precipitating non-solvent to be added—that is, the appearance of turbidity—was not adequate, since much too large a fraction had been brought down.

Step 2

The major fraction from the above (3.106 g.) was dissolved in 311 ml. of chloroform for refractionation. It was intended to dilute this solution with hexane to the concentration existing just before this fraction had come down, and then to add a smaller excess of hexane. When 1,000 ml. of hexane had been added, slowly and with agitation, the solution became slightly turbid. After 24 hrs., the turbidity had not increased, and no material could be removed from the solution by centrifugation. A 130-ml. portion of hexane was added, but in another day the turbidity increased only slightly, if at all, and still no material could be centrifuged from the solution. Since the hexane concentration was now considerably above that at which this sample had previously been precipitated, only 33 ml. were added at this stage. Overnight a heavy, gel-like precipitate formed which proved to be the whole sample (3.052 g., B-42-a). This same behavior was found with two other samples of methyl cellulose in this solvent-non-solvent system.

Step 3

The samples of trimethyl cellulose used in this work were also soluble in pyridine if warmed to 50–60° C, and fraction B-42-a was refractionated by precipitating it from pyridine with water. A 1.5% solution was prepared by dissolving the 3.052 g. of material in 211 ml. of pyridine. This was a little more concentrated than the initial chloroform solutions used above, which were 1% (wt./vol.). Three hundred ml. of distilled water were added, but after standing overnight at constant temperature the solu-

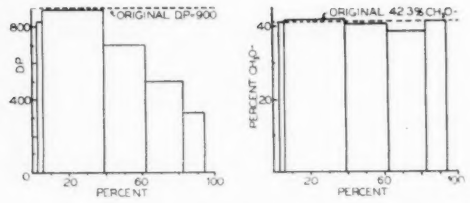


FIG. 2. *D.P. and methoxyl content of fractions obtained from trimethyl cellulose, using the scheme shown in Figure 1.*

tion showed no turbidity. Then 900 ml. of water were added until a milkiness became apparent. When the solution was warmed slightly (5°–10° C), as is frequently recommended to redissolve the precipitate and allow it to come down a second time, it was found that the turbidity increased. On stirring and cooling the flask in an ice bath, the turbidity decreased, but the solution could not be completely cleared. The faintly turbid solution was allowed to stand for 8 days, during which the turbidity increased slightly, but no precipitate formed nor could any material be centrifuged down. An additional 300 ml. of water did not produce overnight any material which could be separated out.

At this point the solution was moved from the constant-temperature room to a stand above a warm-water bath where the air temperature was 30°–35° C. After 2 days, it was possible, with difficulty, to centrifuge off a gelatinous precipitate. Prolonged centrifuging was required. This fraction (B-46-a), after washing with water and drying, smelled very strongly of pyridine. After three reprecipitations from chloroform, each followed by vacuum desiccation over phosphorus pentoxide, the sample no longer smelled of pyridine, and it weighed 2.158 g.

The remainder of the material in solution was coagulated by heating on the water bath and slowly separated out by centrifugation. This sample had to be freed of pyridine as before; it weighed 0.784 g. (B-46-b).

Step 4

The larger of these two fractions was refractionated from pyridine by controlling the temperature as well as the composition of a pyridine-water solution. The sample (B-46-a) was put into a 1-liter, 3-neck flask fitted with a condenser, stirrer, and dropping funnel, and was mounted in a constant-temperature bath controlled to ± 0.5° C. It was dissolved by adding 200 ml. of pyridine and by stirring overnight at 50° C. Then 100 ml. of water were added dropwise, producing a faint but distinct cloudiness in the solution. It was cooled to 0° C for 4 hrs. with continued stirring and then heated to 50° C again. Upon centrifugation the precipitate separated out rapidly and completely. After washing with water and drying, the precipitated material (B-50-a) did not have the pyridine odor of the samples above.

The clear, supernatant solution was returned to the flask, 67 ml. of pyridine-water solution of the proper concentration being used to effect the transfer. Then 200 ml. of water were added, but only a faint cloudiness resulted. The temperature was raised to 55° C and maintained overnight, but practically no material could be centrifuged off the next day. Dilution with 2 liters of water produced no precipitate at 55° C, but on the water bath at about 80° C a flocculent precipitate formed which was collected after most of the solvent had evaporated (B-51-a, 0.889 g.).

Analysis of Fractions

The D.P.'s and methoxyl contents of these fractions are shown in Figure 2. The two fractions separated in chloroform-hexane are a low-molecular-weight sample of the same methoxyl content as the original, and a small sample of slightly lower methoxyl content and D.P., which was the first to precipitate. It appears likely that the latter may have come out of the solution first by association of chains through the agency of the free hydroxyl groups on them, as proposed by Staudinger and Reinecke [5] for ethyl cellulose in benzene.

The three central fractions separated in pyridine-water mixtures have the expected trend in molecular weight, with solubilities as shown in Table I, but there is a parallel trend in methoxyl content, indicating that separation is also occurring because of this difference.

TABLE I. FRACTIONATION IN PYRIDINE-WATER SYSTEM

Sample No.	Solubility	D.P.	% CH_3O–
B-50-a	Least soluble	891	43.5
B-51-a		700	41.1
B-46-a	Most soluble	497	38.5

The least methylated material is the most soluble, as suggested by the fact that the maximum water-solubility of methylated cellulose is at 25% to 30% methoxyl content.

The weighted-average methoxyl content of the fractions is 41.6%, which is in fairly good agreement with the figure for the original sample, 42.3%, although the difference is large enough to suggest the definite possibility that the samples were not all completely freed of solvent. The weighted average of the D.P.'s is 694, which is a serious discrepancy from the original D.P. of 900. It is almost impossible that this difference should be caused by a high molecular weight for the small insoluble fraction or for the lost material. It was undoubtedly due to the degradation of the material during the fractionation. Since solutions of trimethyl cellulose in chloroform had been kept for several weeks without significant change in viscosity, the indications are that the breakdown occurred in the pyridine-water solutions. The general susceptibility of cellulosic materials to oxidation in strongly basic media supports this conclusion. Differences in viscosity-molecular weight due to the fractionation itself would have the opposite effect from that observed—that is, the weighted average would be above the original.

To summarize, the following difficulties have been found which make methyl cellulose an unsuitable derivative for fractionation studies in chloroform-hexane or pyridine-water systems:

1. Turbidity cannot be used as a guide to the incipient precipitation of a fraction in either system.

2. When precipitation occurs, such a large fraction is obtained, even with small increases in non-solvent, that a "cooperative effect" seems probable. The few first precipitating molecules are able to drag down most of the material with them as they fall through the solvent. There remains the possibility that this material was actually very uniform at this stage and that this behavior is more or less to be expected. This does not change the fundamental conclusion that this system is not a good one for determining whether this is true.

3. It is difficult to free the fractions from pyridine, especially when the fractionation is done at room temperature.

4. Serious degradation of the material occurs in pyridine-water solution.

5. In both systems, but more particularly in the pyridine-water, the separation is on the basis of methoxyl content as well as chain length.

Solubility

The current state of knowledge about the solubility of polymers has recently been reviewed by Spurlin [4]. For a long time the ready solubility of most polymers was thought to be incompatible with the existence of large molecules in solution, since the force promoting dispersion was only thermal agitation. It has come to be realized, however, that because of the flexibility of most polymer chains, they may behave segmentally in the solution process, so that the large attractive forces between polymer molecules, which hinder solubility, may be overcome gradually. When a polymer is placed in a solvent the internal pressure of which is approximately the same as that of the polymer, the links of the polymer chains are separated one by one from their positions next to other polymer chains. With a solvent the internal pressure of which is nearly the same as that of the polymer, there is no energy difference favoring one neighborhood or the other for the polymer segment, so that thermal energy and the entropy effect due merely to the size of the polymer molecules are sufficient to produce a highly swollen structure and eventual solution. The solubility behavior of flexible polymer molecules can be studied and interpreted fairly well with the same concepts which are useful with solutions of molecules of lower molecular weight.

Crystalline polymers, particularly those with comparatively stiff chains such as cellulose derivatives, are more generally insoluble because of their reduced flexibility and the essential nature of their crystallization, which means that there must be a heat effect on solution. In order to dissolve such a molecule it is necessary to melt the molecule from the crystal. Therefore, such polymers usually do not dissolve except in solvents which can furnish the required energy by solvation. Sometimes it is necessary to use multicomponent solvents, one component of which swells and solvates the polymer while the second provides a solvent of proper cohesive energy density (C.E.D.) for solution of the complex.

Cellulose is insoluble in ordinary solvents but dissolves with solvation or complex formation in such solvents as strong mineral acids, very strong organic bases, and aqueous cuprammonium hydroxide. As the hydroxyl groups become methylated, the hydro-

gen bonding is reduced and the strength of the interchain forces is changed. At some stage of substitution, the solvation of the remaining free hydroxyl groups is sufficient to make the material water-soluble. The point at which this occurs varies with the chain length; very low-D.P. materials are water-soluble with about a 12% methoxyl content, while the highest-D.P. material obtained from native cotton is most soluble with about 25%. Solution is effected in the cold, ice and water mixtures being most effective. If the temperature is increased, the solvation is reduced and at about 70°C the methyl cellulose is precipitated from the solution. The cohesive energy density of water is so different from that of the unsolvated solute that the latter cannot remain in solution.

When substitution of the hydroxyl groups is continued above this range, the solubility in water decreases and the solubility in organic solvents increases. The material used in this work (with a D.P. of about 900 and with 42.5% to 43.5% CH_3O—) was insoluble in water, but was readily soluble in chloroform. It was immediately swollen to a thick gel which could be dispersed into a clear solution with a moderate amount of shaking. It was similarly swollen by pyridine at room temperature, but not to the point that the fibrous structure was disrupted. After several days of shaking, the material could still be recovered from the pyridine in fiber form. On warming to 50°C, pyridine brought about solution with about the same ease as did chloroform. On cooling to room temperature, or even to 0°C, there was no precipitate. Trimethyl cellulose was likewise swollen by anisole, very much as with chloroform and pyridine, but up to 100°C anisole does not show evidence of being able to continue the swelling until solution results.

Chloroform, pyridine, and anisole have approximately the same C.E.D. and the latter two are as polar or more polar than chloroform. The polarity should be some measure of their ability to solvate the macromolecule. Since this is apparently not so, it would imply that some other factor, possibly a steric effect resulting in an optimum action by a molecule of a given size or shape, is concerned.

When chloroform or pyridine solutions are heated, even to boiling, there is no precipitation of trimethyl cellulose as there is with water solutions of the partially methylated materials. At higher temperatures, the solvation in the organic solutions is reduced as in the former case, at least to some extent, but, even so, the C.E.D. of the solvent is sufficiently close to that of the less solvated solute so that it does not precipitate. For the same reason a chloroform solution of trimethyl cellulose does not precipitate upon essentially infinite dilution with benzene, the C.E.D. of which is approximately the same as that of chloroform and presumably of trimethyl cellulose also. However, on dilution with a solvent of very different C.E.D., as with hexane in the fractionation described above, all of the solute can be thrown out of the solution. The large amount of hexane required indicates that reducing the solvation of the polymer molecules, rather than changing the C.E.D. of the solvent, is the first step as the dilution proceeds, and that when it is reduced sufficiently the molecules find themselves in a solution of unfavorable C.E.D. and precipitate. The reduction of solvation by dilution can be considered to be caused by an equilibrium between the molecules bound by solvation and those free in the non-solvent diluent. As the volume of the latter is increased, the number of solvating molecules is reduced.

When pyridine solutions have been diluted with water to the verge of precipitation, heating the solution will precipitate the solute. Solvation of the methyl cellulose, reduced already by dilution, is further lowered by the rise in temperature, and the change in C.E.D. which had occurred on dilution is sufficient to cause the material to come out of solution. Chloroform solutions similarly diluted with hexane do not show this behavior and are not precipitated, even by boiling. If this is to be interpreted as indicating that the chloroform-methyl cellulose complex is more stable than that with pyridine, it could be correlated with the different solvent powers of these two solvents, and is further indication that dipole moment is no reasonable measure of solvating effectiveness.

It is apparent that the general behavior of methyl cellulose in various solvents can be understood quite generally in terms of the concept that the formation and existence of a solvation complex is the governing factor in its dissolution and precipitation. Solvents the C.E.D.'s of which are approximately the apparent C.E.D. of methyl cellulose (about 9.1 cal.$^{\frac{1}{2}}$ cc.$^{-\frac{1}{2}}$) swell the material without disrupting the fiber or crystalline structure. If they are able to solvate the molecules, the swelling continues until an apparently molecular solution results. Solvents may be divided into three groups with respect to their

TABLE II. SOLUBILITY OF TRIMETHYL CELLULOSE

Solvent	C.E.D.* (cal.$^{\frac{1}{2}}$ cc.$^{-\frac{1}{2}}$)	Dipole (Debye units)	Solubility
n-butyl ether	7.2	1.18	Insoluble, no swelling
n-hexane	7.3	0.0	Insoluble, no swelling
Ethyl ether	7.7	1.2	Insoluble, no swelling
Carbon tetrachloride	8.6	0.0	Insoluble, no swelling
Toluene	8.7	0.34	Insoluble, strong swelling
Benzene	9.0	0.0	Insoluble, strong swelling
n-butyraldehyde	9.0	2.6	Insoluble, slow swelling
Anisole	9.1	1.2	Insoluble, strong and rapid swelling
Trichlorethylene	9.1	0.94	Insoluble, moderate swelling
Chlorobenzene	9.2	1.6	Insoluble, strong and rapid swelling
Chloroform	9.2	1.2	Soluble
Acetone	9.8	2.9	Insoluble, no swelling
Acetic anhydride	9.6	2.0	Insoluble, no swelling
Isopropanol	9.8	1.7	Insoluble, no swelling
Pyridine	10.0	2.2	Strong swelling cold, soluble warm
Carbon disulfide	10.3	0.0	Insoluble, no swelling
Ethanol	11.1	1.7	Insoluble, no swelling
Methanol	13.0	1.69	Insoluble, no swelling
Water	20.7		Insoluble

* Cohesive energy density.

behavior with methyl cellulose. The solvents of the first group do not swell the material or swell it only slightly because they do not have the proper C.E.D. Both polar and nonpolar solvents, such as water, hexane, and acetone, belong to this group. Those in the second group have the proper C.E.D. but are incapable of forming solvation complexes which will overcome the crystalline nature of the material. This may be because they are nonpolar, as benzene, for example, or because of some other factor, possibly a steric one, which must be the case with anisole or chlorobenzene. These solvents usually swell the fiber to a marked extent by penetrating the amorphous regions, but do not permanently disrupt its structure. The third group has the C.E.D. and solvating ability to swell the fiber to complete disruption and solution. Pyridine and chloroform have the necessary properties.

Table II indicates the solubility behavior of methyl cellulose in some organic solvents. The C.E.D.'s were calculated with the assumption that

$$\text{Internal pressure} = \left(\frac{\partial E}{\partial V}\right)_T \approx \frac{L_v}{V},$$

using Hildebrand's Rule to estimate the latent heat of evaporation (L_v) from the boiling point [1]. It is apparent that solvents the internal pressures of which are about 9.1 cal.$^{\frac{1}{2}}$cc.$^{-\frac{1}{2}}$ are all able to cause swelling, but that solubility depends on something further, presumably solvation. The controlling nature of the solvation factor is emphasized by the fact that the C.E.D. of pyridine is somewhat higher than the range which causes maximum swelling. This higher C.E.D. must be about right for the solution of the pyridine solvation complex.

Conclusions

1. Chloroform-hexane and pyridine-water are unsuitable systems for the fractionation of methyl cellulose. Turbidity cannot be used as a guide to incipient precipitation in either system. The former strongly tends to precipitate a large part of the solute at once, even when the amount of non-solvent added is small. In pyridine-water, serious degradation occurs, and the separation is caused not only by D.P. differences but also by differences in methoxyl content.

2. Solution of methyl cellulose is effected only by solvents which are able to solvate it strongly, and the ability of solvents to bring about the necessary degree of solvation depends not only on their internal pressure and polarity but also on still another factor, possibly steric.

Summary

Trimethyl cellulose was fractionated from chloroform-hexane and pyridine-water systems. The difficulties involved are described and lead to the conclusion that neither system is suitable for such a fractionation. These difficulties are related to the solubility behavior of methyl cellulose, which is discussed in the light of present theories of polymer solubility.

Literature Cited

1. Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., New York, Van Nostrand, 1946, pp. 479–80.

2. Mehta, P. C., and Pacsu, E., TEXTILE RESEARCH JOURNAL **19**, 699 (Nov. 1949).
3. Schulz, G. V., and Husemann, E., *Z. physik. Chem.* **B52**, 23 (1942); Husemann, E., and Schulz, G. V., *Z. physik. Chem.* **B52**, 1 (1942).
4. Spurlin, H. M., *J. Polymer Sci.* **3**, 714 (1948).
5. Staudinger, H., and Reinecke, F., *Ann.* **535**, 47 (1938).

(Manuscript received August 26, 1949.)

Cellulose Studies

XV. Infrared Spectra of Trimethyl Cellulose, Cellulose, and Starch

Richard Steele and Eugene Pacsu

Contribution from the Textile Foundation and Frick Chemical Laboratory, Princeton University

THE INFRARED absorption spectrum of methyl cellulose has not been reported in the literature. A technique for drying and mounting thin films so that their spectra can be obtained in the dry state is described herein, and the spectra of methyl cellulose, cellulose, and starch are presented.

The films were made by allowing a solution of the material to evaporate on a clean mercury surface. The methyl cellulose films were cast from chloroform solutions of trimethyl cellulose, prepared as described in Part XIII [6]. Cellulose films were prepared by deacetylating cellulose acetate films (cast from acetone solution) by the method of Rowen, Hunt, and Plyler [3]. The cellulose acetate was a commercial, secondary acetate supplied free of plasticizer. The starch films were cast from an aqueous solution of defatted cornstarch which had been autoclaved for 2 hrs.

The spectra were obtained on a Perkin-Elmer recording infrared spectrometer (model 12C) using a rock-salt prism. The calibration curve was prepared from the NH_3, CO_2, and H_2O bands suggested in the manual supplied with the instrument.

A desiccated cell was constructed, to which a dried film could be transferred and the spectrum obtained without exposing the film to atmospheric water vapor. The cell is a simplified model of the one used by Rowen, Hunt, and Plyler [5]. Figure 1 shows the plan of the cell. The end-pieces were machined of brass, the one to the left in the figure being flanged to fit into the track provided on the spectrometer. The length of the cell was such that the air space between the housings of the instrument was snugly filled. Each end had a 20-mm. circular opening, over which a polished rock-salt plate was clamped by a brass plate held in place by spring tension on four bolts.

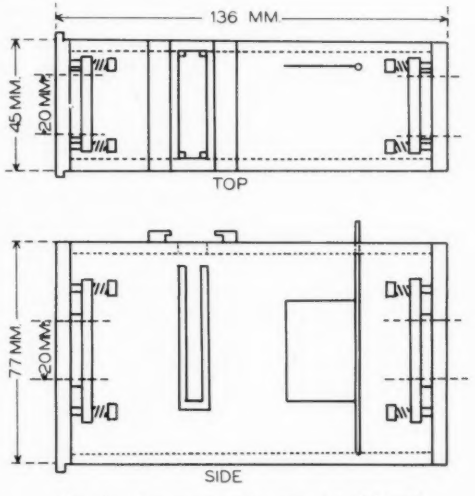


FIG. 1. *Desiccated film cell for infrared spectrometer.*

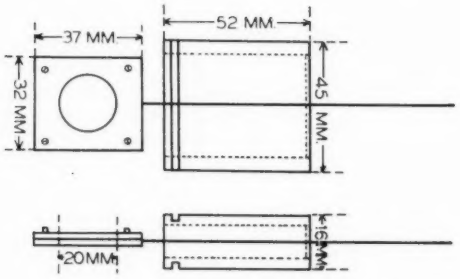


FIG. 2. *Film frame and transfer box.*

The sides, top, and bottom of the cell were of Plexiglas, machined to fit tightly together and to the brass end-pieces. The whole cell was held together by brass bolts. The top was provided with an opening, through which a brass frame holding the sample could slide. On either side of the opening was a brass track for holding the box in which the sample frame was transferred from the desiccator. Tracks of small strips of Plexiglas were provided along the sides of the cell to hold the sample frame in the optical path. The floor of the cell was covered with magnesium perchlorate mixed with a little indicating Drierite. When not in use the cell was stored in a desiccator over these drying agents, with the top opening closed by a small rectangle of Plexiglas slid under the tracks.

In the right-hand end of the cell a shutter was installed so that the zero point of the instrument could be checked periodically by blocking the light path. However, the drift in an alternating-current instrument such as the one used in this work was found to be negligible.

Figure 2 shows the sample frame and transfer box. The frame was soldered to a stiff wire which passed through a hole of very slightly larger diameter in the top of the box. The frame consisted of two brass plates, as shown, held together with small bolts. In preparing for a run, the film sample was clamped between the plates, and the frame was pulled into the box with the wire. A cover of brass and Plexiglas was provided (not shown in the figure) which had a track, as on the top of the cell, and which fitted snugly over the end of the box. The cover was engaged with the open end of the box until about one-fifth of the end was closed, and the whole box was then desiccated *in vacuo* for 48 hrs. or more. Then air was slowly admitted to the desiccator through a magnesium-perchlorate drying-tube, and as soon as the desiccator was opened the top was slid completely over the end of the box. The box was transferred immediately to the cell by sliding it into the track provided, simultaneously pushing the covers off the cell and off the box. In this position the sample frame could be lowered into the optical path of the instrument or removed from it by means of the wire.

Spectrum and background tracings were obtained on the same paper by running a portion of the spectrum tracing first, backing up the paper, and running the background at the same amplifier gain. In order to simplify the calculation from the tracing, it was necessary to synchronize the pips on the two tracings, which are put in automatically at each tenth of the arbitrary units on the wave-length drive. The whole tracing was obtained in several sections so that a maximum amplifier gain could be used in each section. The 2–3-micron region spectrum tracing was run as soon as possible after the sample was transferred in order to decrease the chance of atmospheric water vapor entering the cell around the wire and affecting the result.

The transmissions at various points on the wave-length drive were calculated from the tracing, using a triangular divider [7] made of Plexiglas calibrated to read directly in percent. From the percents transmission and the wave lengths read from the calibration curve, the spectra shown in Figures 3, 4, and 5 were constructed.

Infrared spectra in the region examined have been previously reported for cellulose by Herzog and Laski, Stair and Coblentz, and Rowen, Hunt, and Plyler [3]. Herzog and Laski studied the absorption from 2 to 9 microns of cellulose prepared by denitrating a nitrocellulose film with ammonium sulfhydrate. They attributed bands at 2.9 and 6.0 microns to the fundamental and overtone of —OH rocking, and bands at 3.35 and 7 microns to CH_2 groups. A weak band at 4.6 microns was assigned to the carbonyl group.

Stair and Coblentz examined cellophane and a number of thin, natural cellulosic membranes, such as pokeweed pith and onionskin, at wave lengths from 1 to 14 microns. They found two strong bands at 3 and 6.1 microns, which were tentatively assigned to the presence of moisture or —OH groups.

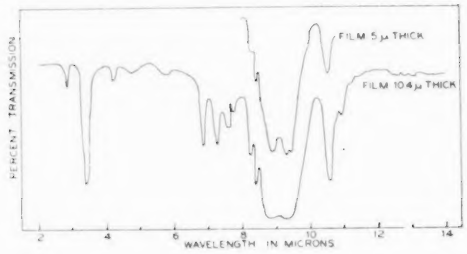


FIG. 3. *Infrared absorption spectrum of trimethyl cellulose.*

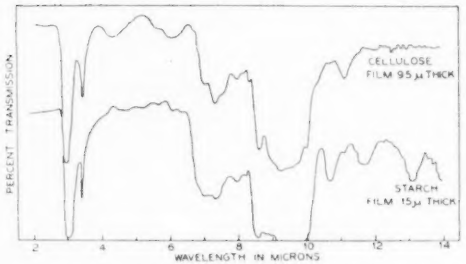


FIG. 4 *Infrared absorption spectra of cellulose and starch.*

Other bands—*e.g.*, at 3.45 and 6.9 microns—were found which were typical of hydrocarbons.

Rowen, Hunt, and Plyler dried their films and ran the spectra in a desiccated cell similar to that described above. They have published the spectrum of a film 2.8 microns thick prepared by deacetylating cellulose acetate. They attribute a 2.8-micron band to —OH vibration and the broad band at 9.5 microns to C—O bonds.

The spectrum in Figure 4 confirms all the chief bands in the spectrum obtained by Rowen, Hunt, and Plyler, and the general absorption which they show in the 6.7–7.7-micron region has been somewhat further resolved into a complex set of bands. The band at 11.1 microns is also considerably larger with the thicker film on which the present spectrum was obtained. The 6.0-micron band found by Herzog and Laski and by Stair and Coblentz is missing in the spectra of dried films and is probably correctly assigned to water in the earlier spectra.

Nothing has been published on the infrared spectrum for starch in this region. The spectrum is remarkably similar to that for cellulose from 2 to 10 microns, although there is generally poorer resolution because of the thicker film. Nor has anything on the spectrum for methyl cellulose previously been reported in the literature.

The following discussion has been written with frequent consultation of several works [2], detailed reference to which would be almost impossible.

The heavy band at 2.92 microns for cellulose and starch has undoubtedly been correctly assigned to the —OH stretching vibration, and, as would be expected, its size is greatly reduced for trimethyl cellulose. The fact that it still occurs for the latter indicates that the hydroxyl groups which apparently so strongly resist methylation in cellulose are actually present and have not been eliminated by becoming involved in ether-type cross-linkages [4] or by other chemical reactions. There is a possibility that this could be demonstrated more fully if a quantitative infrared technique were developed to show that the actual theoretical number of —OH groups were

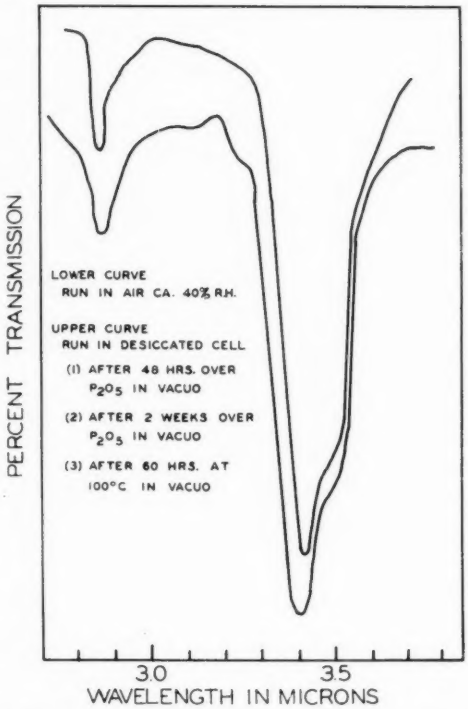


FIG. 5. *Effect of continued drying on the infrared absorption spectrum of trimethyl cellulose in the 2.7–3.7-micron region.*

present. Figure 5 shows that the absorption is probably not attributable to bound water, since more and more drastic drying does not reduce the absorption further.

In methyl cellulose the —OH group appears not to be shifted quite so far as it is in cellulose itself from the position it is normally assumed to have for unperturbed O—H bonds at 2.7 microns. Its center was measured to be at 2.86 microns, compared to 2.92 for cellulose. If these hydroxyl groups are not methylated because of steric hindrance where the chains are pinched together by cross bonds, it is to be expected that they would still be involved in hydrogen bonds, as appears to be the case. There is a possibility that these groups are hydrogen-bonded to ether oxygens in the methoxyl groups. This would be sterically difficult in highly ordered regions, and if it occurs in an amorphous portion it is difficult to understand why they cannot be methylated. A structural basis for the cause of this effect, rather than inaccessibility due to crystallinity differences, is indicated by the work of Barsha and Hibbert [1], who were unable to reach the theoretical methoxyl content by dissolving and reprecipitating the almost completely methylated product and then remethylating it.

The three or more bands in the 6.7–7.7-micron region of the cellulose and starch spectra are probably due to alcoholic C—O bonds. In methyl cellulose they are replaced by three more well-defined absorption maxima at 6.94, 7.26, and 7.64 microns. The 6.94 band is a harmonic of the 3.4-micron C—H band, and the 7.28 band corresponds closely to a band usually found in compounds bearing methyl groups. The 7.64 band corresponds to an apparent maximum in the complex structure of the cellulose spectrum in this region.

The heavy, complex absorption at about 8.5 to 10 microns in each spectrum is attributable to vibrations involving C—O—C bonds in the skeleton of the molecule. Very definite changes occur in this region on methylation which may be due to the new C—O—C bonds produced.

The strong band at 10.56 microns for methyl cellulose is typical of one found with compounds having a CH_3O— group and can probably be assigned to it. It is in a comparatively clear part of the spectrum and of moderate strength, which might make it useful in devising a quantitative method for measuring the number of methylated and unmethylated hydroxyl groups.

The cellulose and starch spectra differ in the region above 10.5 microns, and it is presumed that this is due to the configurational difference between α- and β-glucose residues. The spectra of sufficient reference compounds in the carbohydrate series are not available to establish this. The region from 10.5 to 25 microns may prove to be the most interesting for further infrared study on polysaccharides.

Summary

A technique for mounting films and obtaining their infrared spectra in a dry state is described, and the spectra of trimethyl cellulose, cellulose, and starch are presented and discussed.

Literature Cited

1. Barsha, J., and Hibbert, H., *J. Am. Chem. Soc.* **58**, 1006 (1936).
2. Herzberg, G., "Molecular Spectra and Molecular Structure." New York, Prentice Hall, 1939; Barnes, R. B., Gore, R. C., Liddell, U., and Williams, V. Z., "Infrared Spectroscopy, Industrial Applications and Bibliography." New York, Reinhold, 1944; Faraday Society, "Application of Infrared Spectra to Chemical Problems, A General Discussion." London, Gurney and Jackson, 1945.
3. Herzog, R. O., and Laski, G., *Z. physik. Chem.* **121**, 136 (1926); Stair, R., and Coblentz, W. W., *J. Research Natl. Bur. Standards* **15**, 295 (1935); Rowen, J. W., Hunt, C. M., and Plyler, E. K., TEXTILE RESEARCH JOURNAL **17**, 504 (1947).
4. Karrer, P., and Escher, E., *Helv. Chim. Acta* **19**, 1192 (1936).
5. Rowen, J. W., private communication.
6. Steele, R., and Paesu, E., TEXTILE RESEARCH JOURNAL **19**, 771 (1949) (this issue).
7. Willis, H. A., and Philpotts, A. R., *Trans. Faraday Soc.* **41**, 187 (1945).

(*Manuscript received August 26, 1949.*)

The Preparation and Properties of Alkali-Soluble Metal Carboxymethylcellulose Fibers*

J. David Reid and George C. Daul

Southern Regional Research Laboratory,† New Orleans, Louisiana

A QUICKLY SWELLABLE, partially carboxymethylated cotton yarn has been described [13, 14] and patented [15] by the authors. The alkali-soluble fibers described in the present paper were developed as a result of the same work. The object of the present paper is to call the attention of industry to the possibilities of these soluble fibers.

Low-viscosity, commercial carboxymethylcellulose was used in most of the present work. This material is generally available in the form of the sodium salt which has a substitution of about one acid group per glucose unit. A material with greater substitution would have been of considerable interest but was not available. A patent was issued to Dreyfus [4], which describes production of a highly substituted carboxymethylcellulose, soluble in acetone, containing approximately two acid groups per glucose unit. The authors, however, have been unable to obtain such substitution by the method indicated, which consists of kneading cellulose with monochloroacetic acid and powdered sodium hydroxide. It was found possible to obtain a substitution of approximately two acid groups per glucose unit by treatment with sodium hydride, as will be described. The product, however, was insoluble in acetone.

In the preparation of partially carboxymethylated cotton fabrics, excellent rotproofing was obtained by preparing certain metal salts of the material [13]. In order to study more adequately the properties of these materials, a number of metal salts were prepared using the soluble commercial carboxymethylcellulose. It was observed that some of these salts had excellent fiber-forming characteristics, although all were soluble in dilute alkali.

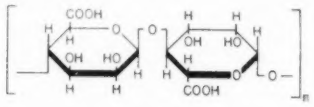
Ordinarily, cellulosic fibers which are soluble in alkali are not of much interest to the technologist. However, in England a soluble "textile from seaweed"—that is, a disappearing alginate fiber—has been developed recently. This is used as a reinforcing fiber during weaving, with subsequent solution with dilute alkali, to obtain extremely light woolen material or unusual patterns with cotton. Descriptions of the fiber in this country [3] have interested the cotton weaving industry because of the variety of novel effects possible with it. Although sodium carboxymethylcellulose should be similar to the alginate, little work appears to have been done to use it in producing a comparable fiber. The excellent review on the uses of carboxymethylcellulose by Hollabaugh, Burt, and Walsh [7] mentions some patent literature on films and filaments, but the data are meager and mainly confined to such preparations as the acid film from the sodium salt. After the present work was done, a patent appeared, granted to Hager and Bock [5] for the alkali-insoluble zirconium fiber, in which other heavy-metal insoluble fibers were mentioned. Their products are described as having been made from alkali-soluble (not water-soluble) carboxyethylcellulose, containing less than 0.5 carboxyethyl-group substitution per glucose unit, which may account for the alkali insolubility and the weakness of the fibers as compared to the fibers to be described in this paper.

The problems of formation of the fibers described herein were considered in the light of work done by Speakman and others [16] in England on the alginate fibers. Although there is considerable argument on the subject of the structure of alginic acid,

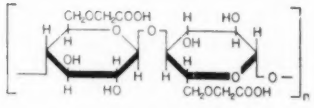
* Presented at the 115th meeting, American Chemical Society, Symposium on Properties and Structure of Natural and Synthetic Fibers, San Francisco, California, March 29, 1949.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

it is, according to Astbury [2] and to Lunde *et al.* [8], a polymeric *d*-mannuronic acid. Astbury found the difference in the fiber repeat distance to be 8.7 A. instead of the 10.3 A. of cellulose and suggests that in the alginate fibers the glucose rings are linked in the alternative way possible for a non-planar, 6-atom ring. Preston illustrates this conception graphically [12]. The alginic-acid unit and a possible carboxymethylcellulose unit are shown below:



ALGINIC ACID



CARBOXYMETHYLCELLULOSE

It is evident that if these concepts are correct there is a considerable similarity between the structural units of the two materials, the difference being mainly the repeat distance and the additional dimethylene ether linkage in the cellulosic material. The composition of carboxymethylcellulose may be closely controlled and variability in composition and properties is probably much less than that of alginate produced from seaweed.

Although it might be assumed that the data available for alginate fibers could be used in the manufacture of carboxymethylcellulose fibers, this is not the case. As an example, in England fibers are made of the calcium salt of alginic acid, whereas the calcium salt of carboxymethylcellulose is soluble in water and unsuitable for the production of a fiber. It was necessary, therefore, to establish the conditions for the production of carboxymethylcellulose fibers of reasonable strength and to examine their properties.

Experimental Procedure

Carboxymethylcellulose Spinning Solutions

An attempt was made to prepare a carboxymethylcellulose containing not fewer than two acid groups per glucose unit, according to the method patented by Dreyfus [4]. One hundred grams of purified, low-viscosity cotton linters, ground to pass a 20-mesh screen, were added to 185 g. of 50% sodium hydroxide solution in a Waring Blendor and thoroughly mixed. The mass was allowed to stand overnight, after which 111 g. of powdered sodium hydroxide were added, with stirring. Then 126.5 g. of monochloroacetic acid were added slowly, with cooling, and the mixture was allowed to stand 6 hrs. The treatment was repeated twice more, each time using 154 g. of powdered sodium hydroxide and 150 g. of monochloroacetic acid, with several hours' standing between treatments and 2 hrs. between base and acid additions. The product was dissolved in the minimum amount of water and precipitated with ethanol. It was purified by again dissolving in water and precipitating. A portion of the product was converted to the copper salt and was found to contain 12.4% copper [13], which corresponded to a substitution of 0.97 carboxymethyl group per glucose unit.

Since the method gave a much lower substitution than desired, the experiment was repeated approximately as before except that commercial carboxymethylcellulose was used as the starting material. The copper salt of this product contained 16.4% copper, or approximately 1.6 carboxymethyl groups per glucose unit, which was double the 0.8 group originally present.

The reaction of sodium hydride to form alcoholates is well known [6]. Accordingly, 5 g. of purified cotton linters, impregnated with approximately an equal weight of monochloroacetic acid and dried under vacuum, were mixed with 1.7 g. of sodium hydride under xylene. The mixture was intermittently stirred over a 4-day period. The product, dissolved in water and precipitated with ethanol, was converted to the copper salt. It had a carboxymethyl-group substitution of 1.8, as shown by the 17.7% copper content.

Preparation of Highly Substituted Carboxymethylcellulose

A successful preparation of a more highly substituted carboxymethylcellulose was obtained by modifying the method as follows:

Twenty grams of the sodium salt of carboxymethylcellulose, ground to pass through an 80-mesh sieve, were covered with 150 ml. of dry xylene, and

20 g. of monochloroacetic acid were added, with mechanical stirring. After ½ hr., 11 g. of sodium hydride suspended in 50 ml. of xylene was added. There was a vigorous reaction and the flask was cooled with ice water. The mixture was stirred at room temperature for 4 hrs., allowed to stand overnight, and stirred an additional 4 hrs., after which 8.3 ml. of water was added dropwise, with agitation, to destroy excess sodium hydride. Approximately 100 ml. of water was then added to dissolve the product, the xylene was decanted, and the product precipitated as the sodium salt from the water solution by the addition of 500 ml. of ethanol. The product was dried and purified by again dissolving in water, precipitating with ethanol, drying, grinding, and extracting in a Soxhlet apparatus with ethyl alcohol. Five grams of the purified product were converted to the copper salt and analyzed for copper content. This was 19.01%, which corresponds to an average of 2.05 carboxymethyl acid groups per glucose unit. The free acid was easily prepared from the sodium salt by adding a mixture of equal parts of concentrated hydrochloric acid and ethanol to the solution of the sodium salt and completing the precipitation by the addition of more ethanol. The free acid, with approximately the same substitution as that given by Dreyfus, differed from his by being insoluble in acetone. In fact, none of the methods used above yielded a free acid which was soluble in acetone or other organic solvents, as claimed by Dreyfus.

It is obvious that the use of sodium hydride with an organic solvent is rather impractical and, accordingly, further experiments were confined to the use of the water-soluble, commercially available material containing approximately 0.8 carboxymethyl group per glucose unit. High-, medium-, and low-viscosity materials were available, but solutions containing more than 2% or 3% of the higher-viscosity materials were too viscous for easy spinning. More dilute solutions did not contain sufficient solids for efficient precipitation during spinning. Consequently, except for a few experiments, low-viscosity material, in 5% to 10% solutions, was used exclusively for spinning fibers.

Removal of Particles from Spinning Solutions

It was necessary to obtain clear solutions, free of microscopic, unreacted cellulosic particles, in order to prevent clogging of the spinnerets. Two methods were used to remove these particles: (1) the carboxymethylcellulose solution was made up to the required concentration—such as 7%—and centrifuged at 1,800 revolutions per min. in a small laboratory centrifuge until the fibers settled out, leaving a clear solution; (2) 2% solutions were made, filtered through a medium-porosity, sintered-glass-filter funnel, and then evaporated to the desired concentration by vacuum distillation. In each method the clear solution was deaerated under vacuum just before use.

Spinning Apparatus and Production of Fibers

Laboratory Spinning

Some metal-salt fibers are extremely difficult to work with. In the preliminary laboratory experimental runs, lead acetate was used as the precipitating material because the lead fiber is easily formed and easy to handle, although after drying it tends to become slightly brittle unless plasticized or otherwise treated. It is indeed so easily produced that it might well be used for lecture demonstrations to illustrate the production of filaments similar to rayon. For this preparation, a 100-ml. pipet-like tube was prepared. The outlet tube was bent at a right angle to the enlarged portion and drawn to a large capillary at the end. The reservoir was filled with a 7% solution of carboxymethylcellulose by suction through the capillary end. The reservoir was fastened with the capillary leading down into a beaker of 10% lead-acetate solution at room temperature. This setup allowed bubbles in the solution to rise to the top of the bulb, where they could not cause fiber breaks. Regulated air pressure (10 to 20 lb.) forced the solution out of the tip and the fiber was easily collected. When much air pressure was used, the pipet was wrapped with tape to prevent injury in case of breakage.

For laboratory experiments using metals other than lead, a more complicated apparatus was necessary. This was constructed using a commercial spinneret containing 52 0.1-mm. holes, which was attached, with an appropriate pipe-fitting and a gasket to prevent leakage, to a bronze pipe which served as a reservoir. The precipitating solution was contained in a stainless-steel trough (2 in. × 3 in. × 30 in.). As the carboxymethylcellulose solution was forced through the spinneret (using 20 to 30 lb. air pressure), it coagulated immediately and the

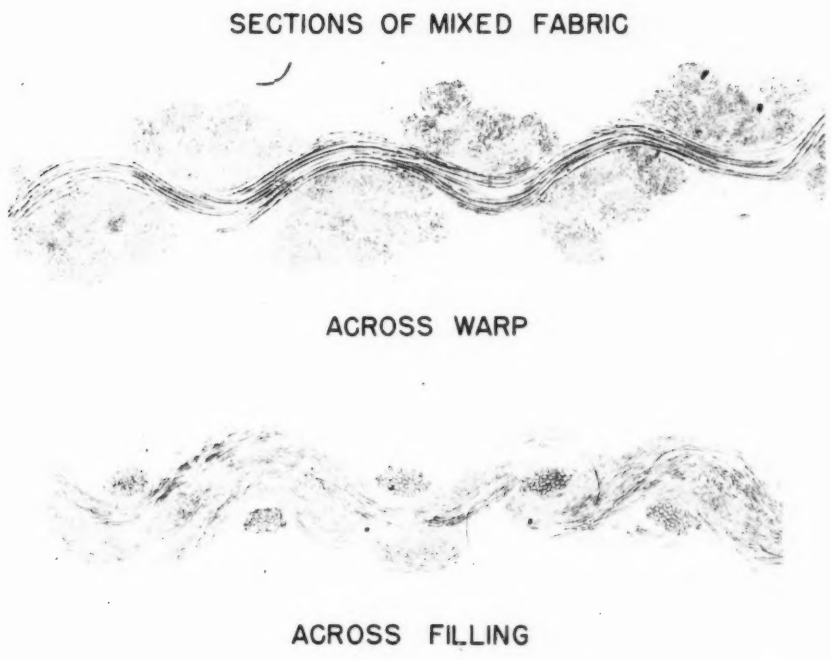


FIG. 1. *Top—Longitudinal section of lead carboxymethylcellulose yarns woven into cotton warp.* Bottom—*Cross section of lead carboxymethylcellulose yarns woven into cotton warp.* (*Magnification 25 ×.*)

fiber formed had to be pulled onto a collecting tube at the other end of the trough. A simple collecting device was made by placing a test tube on a 1-hole rubber stopper over the shaft of a variable-speed electric motor. The other end of the test tube was allowed to rotate in a loose clamp-support. As the fiber was collected on the tube, it was traversed with a glass rod and collected in several layers. This method of collection was convenient because samples for different treatments could be collected on a number of test tubes and the fibers washed or otherwise treated while still on the tubes.

Pilot-Scale Spinning

Trial runs were made on pilot-scale equipment which had been originally developed for spinning peanut protein fibers. This machine has been described by Merrifield and Pomes [11]. A sufficient quantity of fiber was prepared to make some hand-woven cloth using a cotton warp. Cross and longitudinal sections of this mixed cloth are shown in Figure 1.

The Coagulation Bath

A great difference in the character of the yarn was noted with changes in the composition of the coagulation bath. This was particularly true with change in the metal used. A monovalent element such as silver gave extremely weak fibers, presumably owing to lack of a cross-linking agent. A number of metal salts of carboxymethylcellulose have been reported as being insoluble, although presumably solubility will vary somewhat with degree of substitution. For material with approximately 0.8 substitution, the authors have found [13] that lead, copper, aluminum, silver, titanium, thorium, and uranyl salts are nearly insoluble, although the variation of metal content from the theoretical content is considerable in the cases of titanium and thorium in

particular. Analyses were made on each preparation to determine the percentage of metal present. Some of the other factors investigated and typical preparations of fiber are described below.

Effect of Acid on Fiber Formation

Hager and Bock [5] believe that when an alkaline solution of the carboxyethylcellulose is passed into an acid bath containing zirconyl sulfate the ether is converted from an alkali salt to the acid form, which then reacts to form the still more insoluble zirconyl salt. In the present work with the soluble fibers, excess acid interfered with the formation of the metal salts, as was evident from analysis of the fibers for metal content. A quantitative estimation of this difference is shown in Table I, from which it is apparent that increasing amounts of sulfuric acid reduce the copper content of the salt from 11.19%—approximately the theoretical amount—to 2.04%.

TABLE I. EFFECT OF SULFURIC ACID ON THE PRECIPITATION OF COPPER CARBOXYMETHYLCELLULOSE*

$CuSO_4$ (g.)	H_2SO_4 (g.)	Amount of aqueous solution (ml.)	Copper content of salt (%)
23	0	400	11.19
23	2.68	400	5.58
23	5.35	400	2.58
23	10.70	400	2.04

* 100 g. of 7% sodium carboxymethylcellulose solution was precipitated by each of the solutions in a Waring Blendor. Copper was determined as cupric oxide.

Lead Carboxymethylcellulose

As described above, lead fibers were the most easily prepared of all the fibers. The reaction of lead with the carboxymethylcellulose was practically quantitative, the lead content of one preparation being 29.9%, as compared with a theoretical value of 28.8%. The weight of lead in the fiber was a disadvantage in that it greatly reduced the strength as expressed in grams per grex (0.9 × g. per den.). Nevertheless, the ease with which the lead fiber was prepared recommended it for preliminary experiments. Under the conditions used, a 10% lead-acetate solution gave the best results. A 5% solution did not coagulate the carboxymethylcellulose solution fast enough for optimum fiber formation, and a 15% solution precipitated the fiber so rapidly that thorough penetration of the fiber was prevented. Some 3% medium-viscosity and 2.4% high-viscosity carboxymethylcellulose solutions were made up and fibers were spun from them in 10% lead-acetate solution. Although the fibers from the higher-viscosity materials were somewhat stronger, the solutions were too viscous to handle easily with the apparatus at hand. Coagulation baths for the above experiments were kept at room temperature. Some properties of a number of these fibers and the viscosities of the spinning solutions are given in Table II.

For the pilot-scale spinning, lead was selected over other metals as the precipitating agent because it produced fibers that were easier to handle on the

TABLE II. PHYSICAL PROPERTIES OF METAL CARBOXYMETHYLCELLULOSE FIBERS

Metal	Solution concentration†	Precipitating solution	Grex	Tenacity in g./grex Dry	Wet	Knot	Viscosity‡ (poises)
Lead	7% L. V.	10% $Pb(CH_3COO)_2$	397.2	0.87	0.56	0.32	13.71
Lead	3% M. V.	10% $Pb(CH_3COO)_2$	328.0	0.93	0.41	0.17	16.23
Lead	2.4% H. V.	10% $Pb(CH_3COO)_2$	148.2	1.70	0.82	0.79	157.86
Lead*	10% L. V.‡	10% $Pb(CH_3COO)_2$	319.9	1.09	0.68	0	71.59
Copper-aluminum	7% L. V.	5% $CuSO_4$§ 5% $Al_2(SO_4)_3$	279.3	1.28	0.39	0.43	13.71
Copper-aluminum	10% L. V.‡	3% $Al_2(SO_4)_3$ 7% $CuSO_4$	269.8	1.38	0.35	0.47	71.59
Copper-aluminum	10% L. V.‡	5% $K_2Al_2(SO_4)_4$ 5% $CuSO_4$	167.2	1.51	0.23	0.39	71.59
Copper-aluminum	5% L. V.	5% $CuSO_4$ 5% $Al_2(SO_4)_3$	71.8	2.09	**	**	4.60

* This fiber was spun on the pilot-scale machine.
† H. V., M. V., and L. V. indicate high, medium, and low viscosity carboxymethylcellulose.
‡ Containing 0.05% triacetin as a plasticizer.
§ Containing 0.025% emulsified olive oil.
** Not determined.
‡ Viscosities of spinning solutions, determined in a Hoeppler Viscosimeter at 25°C.

TABLE III. COMPOSITION OF MIXED COPPER–ALUMINUM SALTS OF CARBOXYMETHYLCELLULOSE*

Aluminum sulfate 0.2 *N* (ml.)	Cupric sulfate 0.2 *N* (ml.)	Aluminum content (%)	Copper content (%)	Substitution† (%)
0	200	0.00	11.17	100.0
50	150	1.05	6.90	91.1
100	100	2.09	3.99	95.4
150	50	2.87	1.60	84.5
200	0	3.49	0.00	101.4

* 100 g. of a 7% solution of sodium carboxymethylcellulose was added to the precipitating solutions indicated.

† Substitution is based on 0.83 acid group per glucose unit, as determined by the copper analysis; indicates insufficient metal present in the mixed salts.

spinning machine. A 10% solution of low-viscosity carboxymethylcellulose was prepared containing 0.05% triacetin as a plasticizer. The solution was deaerated under reduced pressure and put into the reservoir of the metering pump. It was forced at a rate of 10 ml. of solution per min. through a 40-hole spinneret, the individual holes of which were approximately 0.1 mm. in diameter.

The first fibers produced were too soft to wind on the pickup roller, so the temperature of the coagulation bath was raised to 50° C. This helped to harden the fiber more quickly and made winding possible. Samples were collected on spools and treated in the various ways to be described later.

Copper-Aluminum Fibers

An attempt was made to use a solution of cupric sulfate for the preparation of the copper-containing fiber. The reaction appeared to proceed rather slowly and the fibers formed were soft and gelatinous and, hence, difficult to handle. It was possible to spin a fiber from 10% aluminum-sulfate solution with a little difficulty. The fiber precipitated very rapidly and had a tendency to clog the spinneret. Examination showed that the fiber had a solid skin filled with unreacted carboxymethylcellulose. A mixture of equal parts of 10% solutions of cupric and aluminum sulfates proved to be an excellent precipitating solution. The fiber was the strongest obtained in these experiments. It was a light blue, in contrast to the clear fibers obtained with lead or aluminum. In Table II are given the data on some typical copper-aluminum fibers. The degree of blueness of the fiber changed when the ratio of copper to aluminum was varied in the precipitating bath. It was deemed advisable to vary the concentrations of copper and aluminum in several precipitating solutions and to ascertain quantitatively the amounts of copper and aluminum in the resultant products. Accordingly, a solution of low-viscosity carboxymethylcellulose was prepared and portions containing approximately 10 g. of material each were precipitated without spinning with various concentrations of aluminum and cupric sulfate mixtures, as shown in Table III. Although Speakman and Chamberlain [16] found that with the aluminum salts of alginic acid the aluminum acted as though it had an apparent valence of only 1.38—a phenomenon attributed to steric hindrance—aluminum has a valence of approximately 3 in aluminum carboxymethylcellulose. Aluminum was determined by the method of Willard and Tang [17], the copper being determined afterward electrolytically.

After-Treatment of Fibers

Immediately after spinning, the fibers were in a highly plastic and swollen state and had the property of high extensibility, lending themselves to stretching and other after-treatments. Some fibers were dried under constant tension, which increased the strength slightly and, as might be expected, decreased the elongation.

The fibers had no tendency to adhere to each other as do the alginate fibers, but although no treatment was necessary to prevent adherence, emulsified oils in the coagulation bath, such as those used by Speakman [16], produced a more pleasant hand. Dried monofilaments had a tendency to be slightly harsh, and the addition of 5.0% triacetin as a plasticizer, based on the carboxymethylcellulose present, also produced a softer-feeling yarn.

The metal-cellulosic fibers possess the usual ion-exchange characteristics of metallic salts, and thus the chemical composition of the fibers may be radically changed by after-treatment with various solutions of metal salts. For example, the blue copper-aluminum fiber, if soaked in a solution of aluminum sulfate, loses its blue color by replacement of copper by aluminum. The translucent lead fibers become an opaque white if treated with a sulfate, or light yellow if treated with a soluble chromate. The latter treatment produces a softer fiber whereas the former treatment embrittles the fiber. A 1% ferric-chloride solution gave a reddish-brown color to the

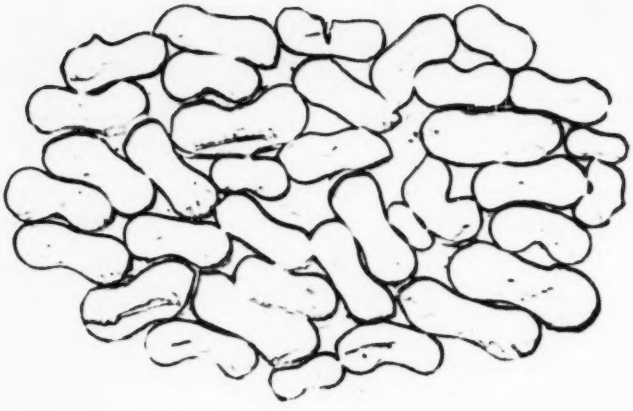


FIG. 2. *Cross section of copper-aluminum carboxymethylcellulose yarn. (Magnification 350 ×.)*

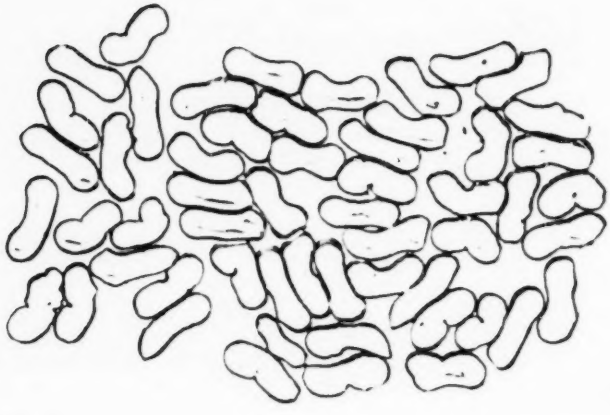


FIG. 3. *Cross section of lead carboxymethylcellulose yarn. (Magnification 350 ×.)*

lead fiber. Such color changes, however, are not of much interest in the use of a soluble fiber.

The metal-cellulosic fibers are not dyed by some of the usual cotton, wool, or acetate dyes; for example, they resist dyeing with such representative dyes as Solantine Blue 4GL, Triazol Fast Red, Celliton Fast Blue, Kiton Red, and Methylene Blue.

Other Characteristics of Metal Carboxymethylcellulose Fibers

In general, the fibers have no unique shape, as shown in cross section. The shape probably depends upon one or more factors, such as rate of extrusion, rate of drying, concentration of solutions, and stretching. Cross sections of copper-aluminum and lead carboxymethylcellulose fibers are shown in Figures 2 and 3, respectively.

The fibers are insoluble in water, weak acids, and organic solvents. They swell about 20% in diameter when wet with water. Measurements made on 100 filaments gave an average diameter of 0.027 mm. when dry and 0.032 mm. when wet. They are readily soluble in 2% solutions of sodium bicarbonate or 1% sodium hydroxide, potassium hydroxide, ammonium hydroxide, ammonium carbonate, and sodium phosphate. They even disintegrate in a mixture of 0.2% soap with 0.2% sodium-carbonate solu-

tion. These solubilities make the fibers useful in combination with wool. Matthews [9] mentions that mild solutions of ammonium carbonate and sodium phosphate do not damage wool and 3% sodium-carbonate solution is used in raw-wool scouring.

Fiber Tenacity and Elongation

The various fibers prepared were tested to determine their wet and dry tenacities as well as their knot strengths [1], the latter being used as a test of the brittleness of the fiber. Some elongations were determined. After conditioning for 24 hrs. or longer at 70°F and 65% relative humidity, the tests were made on 10-in. samples of fiber on an IP-2 Scott tester with a 250-g. carriage. Wet tests were made by immersing the fibers for at least 20 min. in water, after which they were removed and tested immediately.

The elongation of the fiber varied considerably according to the amount of stretching during the preparation; it varied from 2% to 10%, with an average elongation of about 4% at the breaking point.

As shown in Table II, fibers with strengths as high as 2.09 g. per grex were obtained. This is a fairly high value when the rather crude methods of production are taken into consideration. Speakman [16] obtained strengths of about 2 g. per den. (1.8 g. per grex) for the best alginate fibers. A table of average fiber strengths [10], giving values of 3.5 g. per den. (3.2 g. per grex) for cotton and 1.4 g. per den. (1.3 g. per grex) for wool, ranges from a high of 6.7 g. per den. (6.0 g. per grex) for ramie to a low of 0.7 g. per den. (0.6 g. per grex) for casein fiber. It is evident that the metal carboxymethylcellulose fibers described are sufficiently strong for textile usage. Although considerably lower than the dry strengths, the wet strengths and knot strengths compare very well with those for other synthetic fibers. Knot strength, of course, varies with the type of extrusion used, depending particularly upon the thickness of individual fibers. The filaments produced by extrusion through 0.1-mm. holes had an average diameter of 0.027 mm. after stretching and drying. In general, such fibers were easily handled and knotted fairly well.

Summary and Conclusions

It has been shown, both on a laboratory scale by a method suitable for use in lecture demonstration work and on a pilot-size spinning machine, that metal carboxymethylcellulose fibers may be produced from sodium carboxymethylcellulose and suitable metals which are capable of cross-linkage to yield fibers with strengths ranging from 1 to 2 g. per grex. A mixed copper-aluminum carboxymethylcellulose fiber was the most satisfactory from the standpoint of strength, appearance, flexibility, feel, and like characteristics. The fiber is similar to the alginic acid fibers developed in England, and, if commercially developed, should be suitable for novelty fabrics and similar uses where an alkali-soluble fiber is desired.

Acknowledgment

The authors wish to thank Miss A. T. Moore and Miss I. V. deGruy for cross sections and photomicrographs, A. L. Merrifield for assistance in the pilot-scale spinning operations, and W. A. Reeves and R. M. Reinhardt for metal analyses.

Literature Cited

1. A.S.T.M. Standards on Textile Materials, Committee D-13, pp. 321–3 (1948).
2. Astbury, W. T., *Nature* **155**, 667–8 (1945).
3. Cady, W. H., *Am. Dyestuff Reptr.* **37**, 283–4, 286, 289 (1948).
4. Dreyfus, H., U. S. Patent 1,884,629 (Oct. 25, 1932).
5. Hager, O. B., and Bock, L. H. (to Röhm and Haas Co.), U. S. Patent 2,420,949 (May 20, 1947).
6. Hansley, V. L., and Carlisle, P. J., *Chem. Eng. News* **23**, 1332–3, 1380 (1945).
7. Hollabaugh, C. B., Burt, L. H., and Walsh, A. P., *Ind. Eng. Chem.* **37**, 943–7 (1945).
8. Lunde, G., Heen, E., and Øy, E., *Kolloid-Z.* **83**, 196–202 (1938).
9. Matthews' "Textile Fibers," 5th ed. (H. R. Mauersberger, ed.), New York, Wiley and Sons, 1947, p. 592.
10. Meredith, R., *J. Text. Inst.* **36**, T107–30 (1945).
11. Merrifield, A. L., and Pomes, A. F., TEXTILE RESEARCH JOURNAL **16**, 369–77 (1946).
12. Preston, J. M., "Fibre Science," Manchester, England, The Textile Institute, 1949, p. 175.
13. Reid, J. D., and Daul, G. C., TEXTILE RESEARCH JOURNAL **17**, 554–61 (1947).
14. Reid, J. D., and Daul, G. C., TEXTILE RESEARCH JOURNAL **18**, 551–6 (1948).
15. Reid, J. D., and Daul, G. C. (to U. S. Dept. of Agriculture), U. S. Patent 2,448,153 (Aug. 31, 1948).
16. Speakman, J. B., and Chamberlain, N. H., *J. Soc. Dyers and Colourists* **60**, 264–72 (1944).
17. Willard, H. H., and Tang, N. K., *Ind. Eng. Chem., Anal. Ed.* **9**, 357–63 (1937).

(Manuscript received August 10, 1949.)

Note on the Disintegration of Wool in Abrasion Tests*

Herbert F. Schiefer and John F. Krasny

National Bureau of Standards, Washington, D. C.

Abstract

The coating which formed on the abradant when a specimen of wool fabric was abraded and caused the rate of abrasion to increase approximately ten times in three successive tests was examined critically. Microchemical analyses showed that it had the same composition as the unabraded fabric. Infrared absorption curves of the coating and of the powder of the unabraded fabric, ground in a vibratory ball mill, showed the same absorption characteristics. Electron micrographs of the coating showed that it contained extremely small particles, many of which were approximately spherical in shape and about 100 to 200 Å. in size. Similar particles were observed in the abraded debris when the specimen was kept wet with water during the abrasion test, and also in the powder into which the unabraded fabric was ground in the vibratory ball mill. It was concluded that the coating which formed on the abradant consisted of extremely small particles of wool which appear to correspond in shape and size to the elemental structural units (keratin molecules) proposed in recent concepts of the structure of wool.

I. Introduction

Results recently obtained with the Schiefer abrasion testing machine on a wool fabric showed that the rate of abrasion increased approximately ten times when three specimens were tested successively with the same abradant [5]. This effect was obtained with the spring steel blade abradant and also with the pyrex rod abradant. It was found that this tremendous increase in the abrasive action of these two abradants † was caused by a coating which formed on the surface of the abradant. The formation of a coating on the abradant surface has since been observed when a number of other wool fabrics were abraded, and the effect of the coating was always an increase in the rate of abrasion. Tests were made in which the air in the immediate vicinity of the abraded area of the wool specimen and the abradant surface was ionized by an alpha emitter, and it was found that the coating formed as readily on the abradant as it did without ionization of the air. The coating did not appear to form when the wool specimen was kept wet with water during the abrasion test.

In view of the great effect of the coating on the rate of abrasion and the important bearing which this observed effect has on the interpretation of the results of abrasion tests, it seemed essential to examine the nature of the coating very carefully. The results of this study are presented and discussed in this paper.

II. Coating

The coating which forms on the abradant when a specimen of a wool fabric is abraded is brittle, appears to form in ridges, and adheres tenaciously to

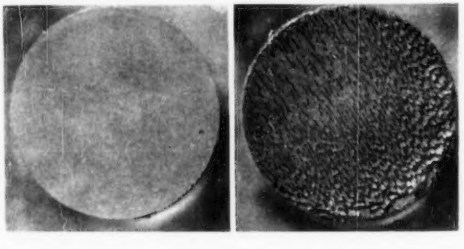


FIG. 1. *Uncoated (left) and coated (right) pyrex rod of abradant.*

* The essential results of this work were presented and discussed by Schiefer at the meeting of Committee D-13 on Textiles of the American Society for Testing Materials, New York, March 16, 1949, and at the meeting of The Fiber Society, Clemson, S. C., April 15, 1949.

This paper will appear also in the January, 1950, issue of the *Journal of Research, National Bureau of Standards.*

† These abradants were found to remain very constant in abrasive action when many other types of textiles were tested. For other abradants, such as sandpaper, emery paper, and cloth, the rate of abrasion decreased greatly in testing several successive specimens with the same abradant.

the abradant surface. A typical example of the coating is shown in Figure 1, where the surface of one pyrex rod of the abradant is completely coated while the other rod, which was located at the outside periphery of the abradant and did not come into contact with the test specimen, is not coated. The diameter of these rods was $\frac{1}{8}$ in. In this test a 2-in.-diameter specimen was abraded so that the periphery of the abraded area always passes through the center of the pyrex rod located at the center of the abradant. This central rod and a group of rods located in concentric circles about it are shown in Figure 2. It is interesting to note that the coating on the central rod appears to build up in radial ridges, whereas the coating on the other rods appears to build up in more or less parallel ridges on each rod. These parallel ridges on the various rods, however, are all radial with respect to the central rod about which the abradant rotates.

In the mathematical solution for obtaining uniform abrasion [4], on which the Schiefer abrasion machine is based, it was pointed out that the direction of the instantaneous relative velocity between any point of the abraded area of the specimen and the abradant is always at right angles to the line which passes through the centers of rotation of the

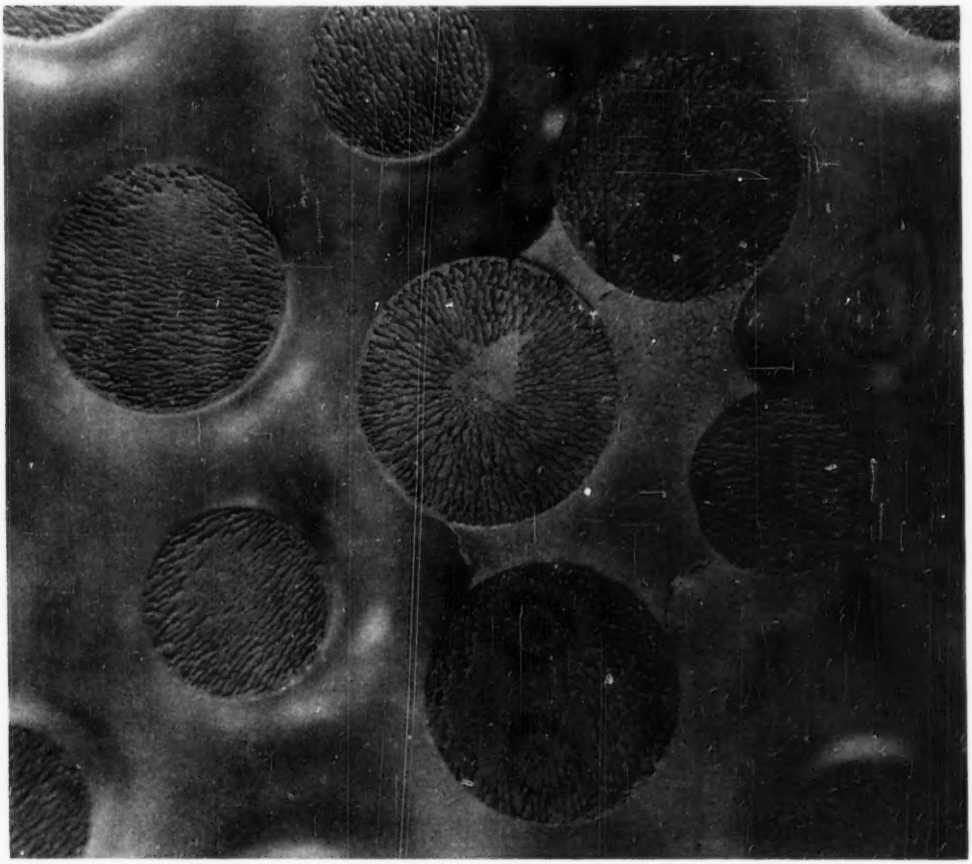


FIG. 2. *Coated pyrex rods of abradant, showing the ridges of the coating converging to the center of rotation of the abradant.*

FIG. 3. *Magnified appearance of the coating on a pyrex rod.*

specimen and of the abradant. All the radii of the central pyrex rod of the abradant coincide with this line once in each rotation. It follows, therefore, that the ridges of the coating on the rods are at right angles to the instantaneous relative velocity between the specimen and the abradant at the instant when each ridge coincides with the line joining the two centers of rotation. This close association between the alignment of the ridges and the direction of the instantaneous relative velocity, when each rod coincides with the line joining the two centers of rotation, suggests that the ridges are probably formed at these instants.

A higher magnification of a small portion of a coated rod is shown in Figure 3. The coating consists of extremely small particles which could not be resolved in the light microscope. It gave a positive test for protein with Millon's reagent.

If the coating on a rod was moistened with water, it was found that it could be very readily lifted from the rod with a sharp razor blade. The layer of coating so removed seemed brittle after it became dry. It dispersed quite readily when it was placed in water and formed a cloudy suspension. It was not difficult to remove and collect a sufficient amount of the coating from the ends of the pyrex rods for microchemical analyses, electron micrographs, and infrared absorption spectra.

III. Microchemical Analysis

The coatings which formed on the abradant when specimens of three different wool fabrics were abraded were removed from the ends of the pyrex rods as described in the preceding section. A microchemical analysis was made of the coating of each

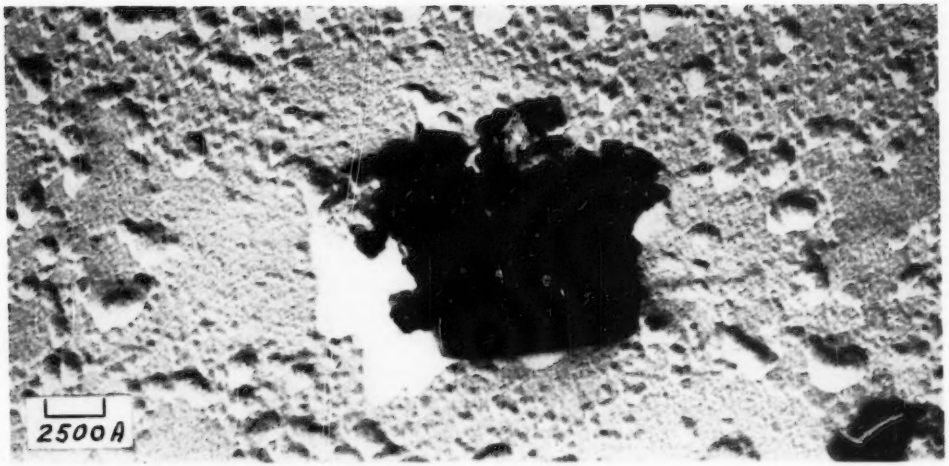


FIG. 4. *Chromium-shadowed electron micrograph of the coating obtained from an undyed wool fabric. (Shadows are white.)*

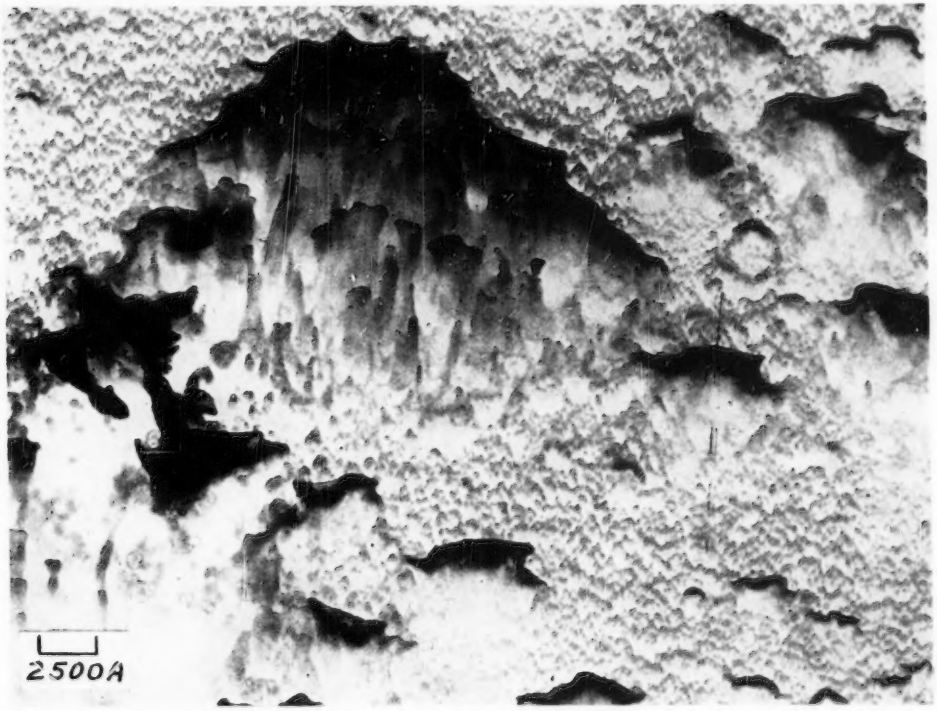


FIG. 5. *Chromium-shadowed electron micrograph of the coating obtained from a blue dyed wool fabric. (Shadows are white.)*

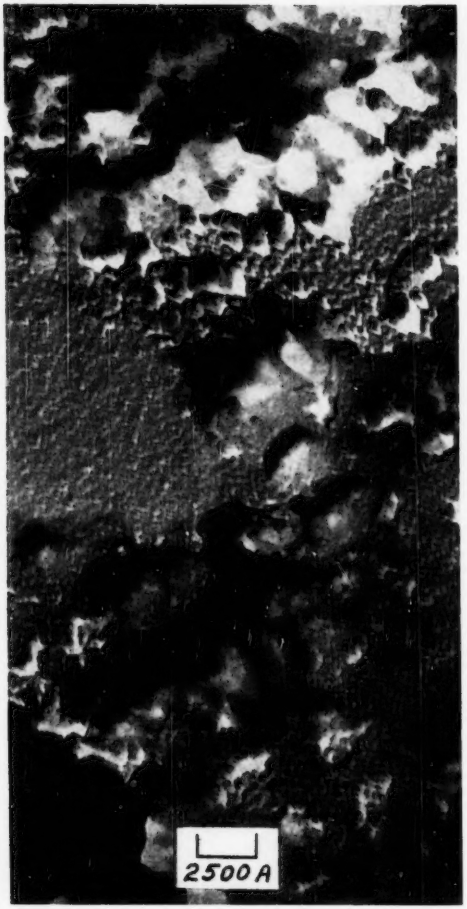


FIG. 6. *Chromium-shadowed electron micrograph of the wet abraded debris from undyed wool fabric. (Shadows are white.)*

FIG. 7. *Chromium-shadowed electron micrograph of the wet abraded debris from blue dyed wool fabric. (Shadows are white.)*

TABLE I. MICROCHEMICAL ANALYSES OF 3 WOOL FABRICS AND OF THEIR COATINGS FORMED ON THE ABRADANT

Description	Hydrogen (%)	Carbon (%)	Nitrogen (%)	Sulfur (%)	Chlorine (%)	Ash (%)	Oxygen (obtained by difference) (%)
Undyed wool, fabric	6.7	46.1	15.0	3.0			29.2
Undyed wool, coating	7.0	45.6	14.5	3.2			29.7
Blue dyed wool, fabric	6.7	46.1	14.3	4.4	none	1.7	26.8
Blue dyed wool, coating	7.1	46.0	13.6	4.2	none	2.4	26.6
Tan dyed wool, fabric	6.8	46.3	15.2	2.8	0.1		28.8
Tan dyed wool, coating	6.8	45.4	14.5	3.3	0.1		29.9

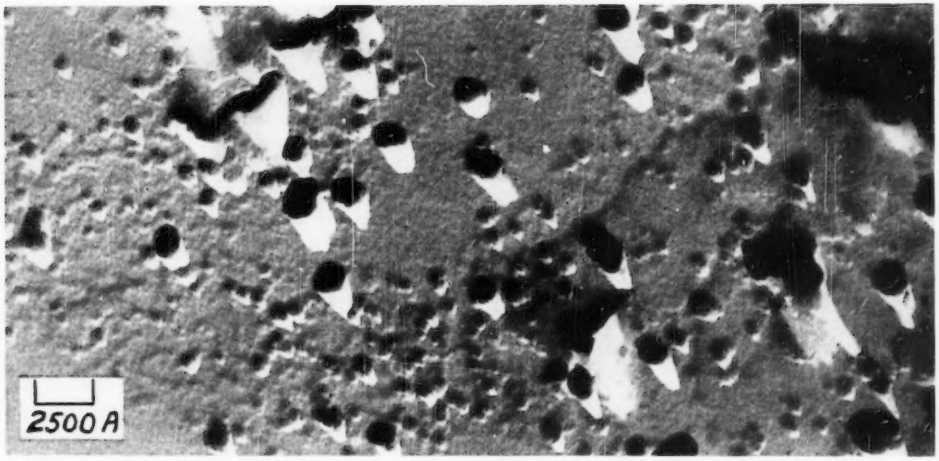


FIG. 8. *Chromium-shadowed electron micrograph of ground powder of blue dyed wool fabric. (Shadows are white.)*

fabric and also of a portion of each unabraded fabric. The results are given in Table I. They show that the hydrogen, carbon, and sulfur composition of the coating is in each instance the same, within experimental error, as that of the unabraded fabric. The nitrogen content of the coating seems to be consistently and significantly lower than that of the fabric. The compositions of the three coatings and of the three fabrics are very nearly alike and are close to the values reported for wool in the *American Wool Handbook*. It is concluded that the coating which formed on the abradant in these tests is composed of extremely small particles of wool abraded off the wool fibers rather than of a resinous or other finishing substance which was added to the wool fibers in manufacture. When asked, the supplier of one of the dyed wool fabrics stated that it contained no resinous finish. No reply was received from the supplier of the other dyed wool fabric.

IV. Electron Micrographs

A small amount of the coating, removed from the abradant, was dispersed in water, and a minute quantity of the dispersion was placed on a collodion film which was shadowed with chromium to enhance the contrast of the electron microscope image. Electron micrographs of the wool particles comprising the coating on the abradant for the undyed and the blue dyed wool fabrics are shown in Figures 4 and 5. It can be clearly seen that the coatings consisted of many small particles which were approximately spherical in shape. Particles 200 Å. in size are definitely resolved and some particles grade down to the particle size of the background, which is of the order of 100 Å. Many of the larger particles may be undispersed aggregates of the smaller particles. Others appear to be larger-sized particles which were abraded off the wool fibers during the abrasion test.*

It was mentioned earlier that the coating did not appear to form on the abradant when the specimen was kept wet with water during the abrasion test. Droplets of water which were thrown off during the wet abrasion test made with the spring steel blade abradant contained very finely dispersed abraded debris. A quantity of these droplets was collected which yielded sufficient abraded material for electron micrographs and for infrared absorption spectra. Electron micrographs of the abraded wool particles which were obtained during wet abrasion are shown in Figures 6 and 7 for the undyed and blue dyed wool fabrics. A large number of very small particles, approximately 100 to 200 Å. in size, can be observed as being produced during the wet abrasion test of these fabrics.

For infrared absorption spectra studies of cellulose, Rowen, Forziati, and Stone ground the cellu-

* In all abrasion tests of wool fabrics, fragments of the wool fibers, scales, and corticle cells constitute part of the abraded debris. These fragments are not considered in this paper.

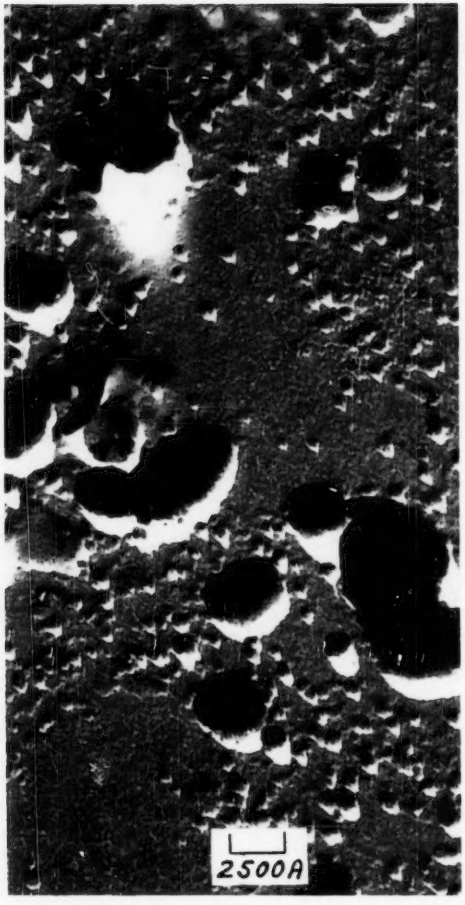


FIG. 9. *Chromium-shadowed electron micrograph of ground powder of blue dyed wool fabric. (Shadows are white.)*

lose into a very fine powder in a vibratory ball mill. The three wool fabrics were ground in the same manner. Electron micrographs of this finely ground powder are shown in Figures 8 and 9 for the blue dyed wool fabric. Although most of the particles are very much larger than 200 A., there are some particles of the order of 100 to 200 A.

V. Infrared Absorption Spectra

Infrared absorption spectra were obtained for the coating which formed on the abradant, for the debris contained in the droplets of water which were thrown off during the wet abrasion test, and for the finely ground powder which was obtained when a small amount of the unabraded fabric was ground in the vibratory ball mill. The infrared absorption spectra obtained under all of these three conditions for each of the three wool fabrics showed essentially the same absorption characteristics. Detailed discussion and interpretation of the infrared absorption spectra of wool are beyond the scope of this paper.

VI. Discussion

The results presented in the preceding sections indicate that wool disintegrates into very small particles during both wet and dry abrasion tests with the Schiefer abrasion testing machine. Some of these small particles are roughly globular in shape and of the order of 100 to 200 A. in size. They appear to correspond to the elemental particles (keratin molecules) recently suggested for the structural units of the protofibrils and matrix of wool [1]. They are also of about the same size as the thickness of the epicuticle, or skin on the wool surface [2, 3], which probably is the same as the smooth outer layer of the wool scales, and which was shown to be worn off during abrasion tests with the Schiefer abrasion machine [6]. During a recent visit to the National Bureau of Standards, Dr. J. R. H. van Nouhuys, Vezelinstituut, T.N.O., Delft, Holland, stated to one of the authors that the Fibre Research Institute had examined the abraded debris under buttons of wool garments and found that in actual wear wool disintegrates into a very fine powder of approximately the same size particles as those which are worn off during the abrasion tests discussed in this paper.

Although complete answers have not been obtained as to why the abradant becomes coated during an abrasion test of a wool fabric, why the abrasive action of the abradant is thereby greatly increased, and how the formation of the coating may be prevented, interesting information was obtained concerning the mechanical disintegration of wool. The very small disintegration products obtained appear to conform in size and shape to the elemental structural units proposed in recent concepts of the structure of wool. It is possible that the results of mechanical disintegration of wool in this type of

abrasion test can provide an additional tool in appraising the effects of chemical modifications and treatments of wool.

Acknowledgment

The authors are indebted to Rolf Paulson, who made the microchemical analyses; to Sanford Newman and Max Swerdlow, who made the electron micrographs; and to John Rowen, Florence Forziati, and Walter Stone, who obtained the infrared absorption spectra.

Literature Cited

1. Farrant, J. L., Rees, A. L. G., and Mercer, E. H., Structure of Fibrous Keratin, *Nature* **159**, 535–6 (1947).
2. Lindberg, J., Allwörden's Reaction, TEXTILE RESEARCH JOURNAL **19**, 43–5 (1949).
3. Lindberg, J., Philip, B., and Gralén, N., Occurrence of Thin Membrane in the Structure of Wool, *Nature* **162**, 458–9 (1948).
4. Schiefer, H. F., Solution of the Problem of Producing Uniform Abrasion and Its Application to the Testing of Textiles, *J. Research Natl. Bur. Standards* **39**, 1–10 (1947); TEXTILE RESEARCH JOURNAL **17**, 360–8 (1947).
5. Schiefer, H. F., Crean, L. E., and Krasny, J. F., Improved Single-Unit Schiefer Abrasion Testing Machine, *J. Research Natl. Bur. Standards* **42**, 481–97 (1949); TEXTILE RESEARCH JOURNAL **19**, 259–69 (1949); *ASTM Bull.*, No. 159, 73–8 (1949).
6. Swerdlow, M., and Seaman, G. S., A Method for the Electron Microscopy of Wool, *J. Research Natl. Bur. Standards* **41**, 231–45 (1948); TEXTILE RESEARCH JOURNAL **18**, 536–50 (1948).

(*Manuscript received September 27, 1949.*)

The Flow Properties of Fibers*

Stephen A. Rossmassler† and Henry Eyring‡

Abstract

A sinusoidal rate of loading is one of the less common ways of testing fibers. A mathematical treatment of the behavior of visco-elastic materials under such conditions is developed, and this theory is applied to data obtained using Nylon 66 monofils. The results indicate that the significant values for the flow process are dependent on the frequency of vibration. An experimental method of obtaining the data necessary is described.

THE WORK described here is concerned with the behavior of polymeric materials when these are subjected to a sinusoidal rate of loading. The theoretical part, based on the principles of absolute reaction rates as applied to viscosity, develops a method of treating experimental data obtained from fibers undergoing longitudinal vibrations, permitting evaluation of the significant constants for the flow process. The experimental part describes a technique for obtaining such data. Optical methods were employed, a weight on the end of the fiber being photographed with a motion-picture camera. The fiber (Nylon 66 monofils) was enclosed in a container which permitted temperature and humidity control.

Theory

The application of a force to a fiber results in the distribution of the force over the various molecular units which are present. In general terms, a unit can stretch elastically, or slip, or do both. This visco-elastic behavior leads to a mechanical model consisting of a pure spring in parallel with a spring-and-dashpot element. In order to describe fully the behavior of a fiber, one such group should be considered for each different molecular unit. Practically, most behavior can be well approximated by one group.

The mathematical treatment of such models, based on the theory of absolute reaction rates, has been presented in detail [1], and analysis has been made of the behavior of fibers, particularly under constant rate of elongation and constant rate of loading [2]. In addition, some work has been done by Tobolsky and Eyring on the problem of a sinusoidal rate of loading, particularly in the case of rubber [3].

A—Derivation of the Equation of Motion

Consider the model shown in Figure 1, when a total force, $F = f_1 + f_2$, is applied and then released. The unit rate of elongation of Unit 1 under the applied stress f_1 is the sum of the rate of elongation of the spring and the rate of elongation of the dashpot, and is given by

$$\dot{\gamma}_1 = \frac{1}{g_1}\frac{df_1}{dt} + K \sinh \alpha f_1, \qquad (1)$$

where $\dot{\gamma}_1 = \frac{d\gamma_1}{dt}$ = rate of elongation; g_1 = spring constant of Unit 1; $\alpha = \frac{V_\lambda}{2kT}$; V_λ = volume of the hole into which the flowing unit jumps; k = Boltzmann's constant; T = absolute temperature; $K = \frac{2\lambda}{\lambda_1}\frac{\kappa}{\kappa}\frac{kT}{h}e^{-\Delta F^\ddagger/RT}$; κ = transmission coefficient (assumed = 1); h = Planck's constant; $\Delta F^\ddagger$ = free energy of activation; R = gas constant; $\frac{\lambda}{\lambda_1}$ = elongation per relaxation process divided by distance in flow direction between relaxing units. For Unit 2,

$$\dot{\gamma}_2 = \frac{1}{g_2}\frac{df_2}{dt}, \qquad (2)$$

but the total rate of elongation of the system is equal to the rate of elongation of each unit:

$$\dot{\gamma} = \dot{\gamma}_1 = \dot{\gamma}_2,$$

and so, if equations (1) and (2) are added:

$$(g_1 + g_2)\dot{\gamma} = \dot{f}_1 + \dot{f}_2 + Kg_1 \sinh \alpha f_1. \qquad (3)$$

* Work done on ONR Project "Creep, Flow, and Failure in Solid Materials," at the University of Utah. This paper was presented before the High Polymer Symposium of the American Chemical Society meeting at San Francisco, April, 1949.

† Graduate student in chemistry, University of Utah.

‡ Dean of the Graduate School, University of Utah.

According to Newton's laws of motion

$$F = f_1 + f_2 = -m\ddot{\gamma} + mg \tag{4a}$$

or

$$f_1 + f_2 = (-m\ddot{\gamma} + mg). \tag{4b}$$

If equation (4b) is differentiated with respect to time,

$$\dot{f}_1 + \dot{f}_2 = -m\dddot{\gamma}; \tag{5}$$

substituting these into equation (3):

$$(g_1 + g_2)\dot{\gamma} = -m\dddot{\gamma} + Kg_1 \sinh(-m\ddot{\gamma} - g_2\dot{\gamma})\alpha. \tag{6}$$

It is now assumed that for small displacements the dashpot behaves linearly—that is,

$$\sinh x = x \quad \text{for small values of } x.$$

Then for small values of $(-m\ddot{\gamma} - g_2\dot{\gamma})\alpha$,

$$(g_1 + g_2)\dot{\gamma} = -m\dddot{\gamma} - Kg_1(m\ddot{\gamma} + g_2\dot{\gamma})\alpha. \tag{7}$$

The solution of equation (7) is obtained by taking $\gamma = Ce^{bt}$, whence

$$Cb(g_1 + g_2)e^{bt} = -Cmb^3e^{bt} - CKg_1m\alpha b^2e^{bt} - CKg_1g_2\alpha e^{bt}, \tag{8a}$$

or

$$b^3 + Kg_1\alpha b^2 + \frac{g_1 + g_2}{m}b + \frac{Kg_1g_2\alpha}{m} = 0. \tag{8b}$$

Equation (7) therefore has the general solution:

$$\gamma = C_1e^{b_1t} + C_2e^{b_2t} + C_3e^{b_3t}. \tag{9}$$

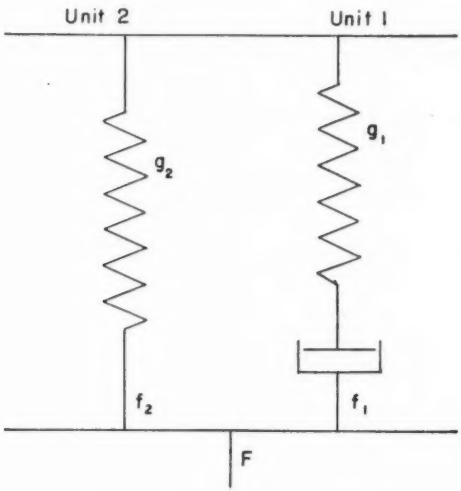


FIG. 1. *Model for visco-elastic behavior.*

This can be written in the more convenient form

$$\gamma = Ae^{-\alpha t}\cos 2\pi\nu t + Ce^{-ct}, \tag{10}$$

which can be compared with experimental data. The discussion of experimental results gives this comparison.

B—Considerations of Energy Losses

The viscous flow which causes damping can be treated as a rate process in the conventional way [4]. The rate of crossing the potential energy barrier is given by

$$k_{\text{net}} = \kappa\frac{kT}{h}e^{-\Delta F^\ddagger/RT}\,2\sinh(V_hF/2\sigma kT),$$

where σ = cross section of the fiber.

The energy loss due to damping of the vibration will be equal to the number of mobile units present $\left(\frac{V}{V_m}\right)$, where V_m = the volume of the flow unit, times the rate of moving (k_{net}), times the energy loss per move $\left(\text{energy} = \text{force} \times \text{distance} = V_h\frac{F}{\sigma}\right)$. Integrating over a full cycle of vibration gives

$$\Delta E = \int_0^{\tau}\frac{V}{V_m}V_h\frac{F}{\sigma}k_{\text{net}}dt \tag{11}$$

or, if the expression for k_{net} is introduced,

$$\Delta E = \kappa\frac{kT}{h}e^{-\Delta F^\ddagger/RT}\frac{V}{V_m}\int_0^{\tau}(V_hF/\sigma) \times 2\sinh(V_hF/2\sigma kT)dt. \tag{12}$$

This is the integral over the complete cycle. If the small asymmetry of a cycle is neglected and the average maximum amplitude A is taken as

$$A = \frac{A \text{ initial} + A \text{ final}}{2},$$

then

$$\int_0^{\tau}f(t)dt = 4\int_0^{\tau/4}f(t)dt,$$

so that equation (12) becomes

$$\Delta E = \frac{8k^2T^2V}{hV_m}e^{-\Delta F^\ddagger/RT}\int_0^{\tau/4}(V_hF/2\sigma kT) \times 2\sinh(V_hF/2\sigma kT)dt. \tag{13}$$

For a sinusoidal motion, $F = -4\pi^2\nu^2mA\cos 2\pi\nu t$,

and if $-\frac{2\pi^2 v^2 mA\,V_b}{\sigma kT} = b$ is substituted in equation (13) for ease of writing,

$$\Delta E = \frac{8k^2T^2V}{hV_m}e^{-\Delta F^\ddagger/RT}\int_0^{\pi/4} b\cos 2\pi vt \times (e^{b\cos 2\pi vt} - e^{-b\cos 2\pi vt})dt, \quad (14)$$

making a change of variable

$$x = 2\pi vt \qquad dt = \frac{dx}{2\pi v}$$

$$\Delta E = \frac{4k^2T^2V}{\pi vhV_m}e^{-\Delta F^\ddagger/RT}\int_0^{\pi/2} b\cos x \times (e^{b\cos x} - e^{-b\cos x})dx. \quad (15)$$

If the exponentials are expanded,

$$e^{b\cos x} - e^{-b\cos x} = 2\left[b\cos x + \frac{b^3\cos^3 x}{3!} + \frac{b^5\cos^5 x}{5!}\cdots\right],$$

equation (15) reduces to

$$\Delta E = \frac{8k^2T^2V}{\pi vhV_m}e^{-\Delta F^\ddagger/RT} \times \int_0^{\pi/2}\left[b^2\cos^2 x + \frac{b^4\cos^4 x}{3!} + \cdots\right]dx, \quad (16)$$

or, letting $\frac{8k^2T^2V^2}{\pi vhV_m} = d$, and integrating termwise,

$$\Delta E = de^{-\Delta F^\ddagger/RT}\left[\frac{b^2\pi}{4} + \frac{b^4 3\pi}{3!16} + \frac{b^6 5\pi}{5!32} + \cdots\right] = de^{-\Delta F^\ddagger/RT}[.786b^2 + .0982b^4 + .00408b^6 + \cdots]. \quad (17)$$

For values of b which occur in practice, three terms of the series give an accuracy of better than 1 percent.

It may be noted that equation (17) is written for a single flow unit. This is adequate since the relaxation time is short, and any flow unit with a much greater value of $\Delta F^\ddagger$ will not flow appreciably in the time available. On the other hand, those units which have a very low $\Delta F^\ddagger$ will flow easily, but will not contribute measurably to the damping since little work is done on them. In other words, at any given vibration frequency there will be only a certain number of flow units responsible for the damping, and all these will have nearly equal values of $\Delta F^\ddagger$.

Experimentally, it is ΔE which is the quantity obtained, and values are chosen for $\Delta F^\ddagger$, V_b, and V_m which when substituted in equation (17) give the best agreement with experiment and with

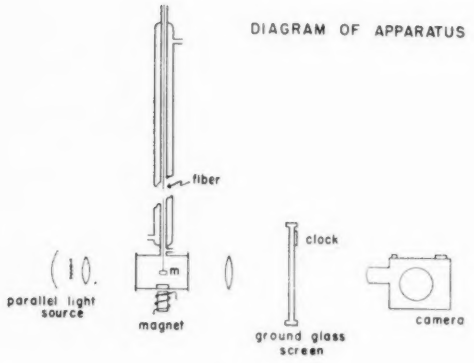


FIG. 2.

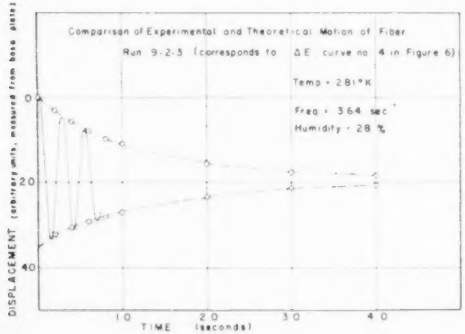

Comparison of Experimental and Theoretical Motion of Fiber
Run 9-2-3 (corresponds to ΔE curve no. 4 in Figure 6)
Temp. = 281°K
Freq. = 3.64 sec⁻¹
Humidity = 28 %
DISPLACEMENT (arbitrary units, measured from base plate)
TIME (seconds)

FIG. 3.

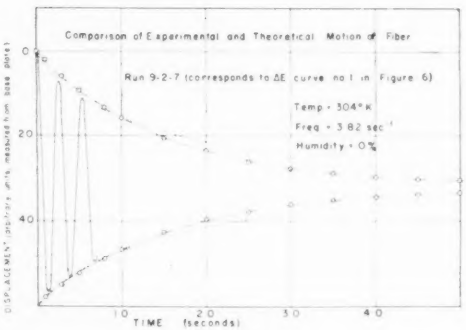

Comparison of Experimental and Theoretical Motion of Fiber
Run 9-2-7 (corresponds to ΔE curve no. 1 in Figure 6)
Temp. = 304°K
Freq. = 3.82 sec⁻¹
Humidity = 0%
DISPLACEMENT (arbitrary units, measured from base plate)
TIME (seconds)

FIG. 4.

TABLE I. DATA FOR EQUATION OF MOTION

Run	Equation	A^*	a^*	$2\pi v$	C^*	c^*	T (°K)	Humidity (%)	σ (cm.²)	m (g.)
8-9-1	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00816	.612	22.2	.00102	1.06	303	32	?	5.17
8-9-2	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00942	.594	22.5	.00070	.916	303	0	?	5.17
9-2-3	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00616	.751	22.9	.00091	1.61	281	28	3.59×10^{-6}	5.17
9-2-4	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00965	.663	25.2	.00087	1.40	282	0	3.59×10^{-6}	5.17
9-2-6	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.01032	.673	24.1	.00065	1.51	304	0	3.59×10^{-6}	5.17
9-2-7	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.01068	.654	24.0	.00079	1.01	304	0	3.59×10^{-6}	5.17
9-2-8	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00797	.738	23.4	.00106	.781	306	0	3.59×10^{-6}	5.17
11-26-2	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00755	.639	27.1	.00099	.248	297	25	2.74×10^{-6}	7.18
11-26-3	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00491	.523	27.4	.00113	.315	296	26	2.74×10^{-6}	4.05
11-26-4	$Ae^{-at}\cos 2\pi vt + Ce^{-ct}$	.00582	.416	26.6	.00031	.228	295	25	2.74×10^{-6}	4.05

* Values given in reduced units.

plastic flow experiments on fibers. In this way the flow constants can be evaluated.

Experimental Procedure

A—Apparatus

The experimental setup is shown in Figure 2. A weight m is attached to the end of a single filament of fiber about 1 meter long (Nylon 66 was the fiber used in all these experiments). The weight is illuminated with parallel light, and the shadow is focused on a ground-glass screen. A motion-picture camera operating at 64 frames per second records the motion of the shadow. A clock, consisting of a synchronous motor geared to make 60 r.p.m., is mounted in the frame of the screen so that each exposure includes a record of the time. The fiber is given an initial displacement by means of an electromagnet which draws the weight down to a fixed horizontal base plate. The base plate appears in the photograph and serves as a reference point for measurement. When the current to the magnet is cut off, the fiber begins its vibrations. Humidity is controlled within the apparatus by evacuating the system and admitting air of known water content. Temperature is regulated by means of a water jacket surrounding the fiber.

The data are obtained by measuring the displacement of the weight from the base plate in the projected picture (a microfilm reader is used). The diameter of the weight serves as a check on the magnification of the system.

B—Results

1. Equation (10) gives the theoretical form of the equation of motion for longitudinal vibrations, based on the assumption of a linear dashpot. Table I summarizes the experimental conditions under which several runs were made and gives the resulting values for the constants in equation (10). The kind of agreement obtained between experiment and theory is illustrated in Figures 3 and 4. Here the curve for the observed motion is plotted as a solid line, and an "envelope" curve drawn tangent to the peaks is dotted. Equation (10) is used in the form $\gamma = Ae^{-at} + Ce^{-ct}$ to calculate the corresponding theoretical values, the cosine function being kept at the maximum value of 1 to simplify computations. The dotted line should then coincide with the theoretical (broken line) curve, both having the harmonic portion eliminated. The figures show that only fair agreement is achieved. This is due to the over-simplification in taking the dashpot as linear.

Qualitative conclusions can be drawn from these data with proper precautions. Since the initial amplitude of vibration affects the amount of damp-

TABLE II. RECALCULATED EQUATION OF MOTION

Run	Equation*	Temp. (°K)	Humidity (%)	σ (cm.²)
8-9-1 (R)	$\gamma = .0060e^{-.581t}\cos(22.2t) + .00049e^{-.141t}$	303	32	Not known
8-9-2 (R)	$\gamma = .0060e^{-.557t}\cos(22.5t) + .00028e^{-.693t}$	303	0	Not known
9-2-3 (R)	$\gamma = .0060e^{-.753t}\cos(22.9t) + .00086e^{-1.61t}$	281	28	3.59×10^{-6}
9-2-4 (R)	$\gamma = .0060e^{-.703t}\cos(25.2t) + .00039e^{-1.71t}$	282	0	3.59×10^{-6}
11-26-4 (R)	$\gamma = .0058e^{-.316t}\cos(26.7t) + .00031e^{-.228t}$	295	25	2.74×10^{-6}

* Constants given in reduced units.

TABLE III. DATA FOR CALCULATIONS BASED ON ENERGY LOSS

Curve	Run	Length of fiber (cm.)	Mass (g.)	Initial amp. (cm.)	Cross section $\times 10^6$ (cm.^{2})	Temp. (°K)	Humidity (%)	Freq. (sec.$^{-1}$)	V_m (cm.^{3}) $\times 10^{21}$	V_k (cm.^{3}) $\times 10^{22}$	$\Delta F_k^\ddagger$ (kg.cal.)
1	9-2-7	114.7	5.17	1.23	3.59	304	0	3.82	2.34	1.73	20.0
2	9-2-4	114.5	5.17	1.11	3.59	282	0	4.00	2.34	1.64	18.5
3	11-26-2	93.7	4.05	.707	2.57	297	25	4.36	2.34	1.18	19.5
4	9-2-3	114.4	5.17	.704	3.59	281	28	3.64	2.34	2.00	18.5
5	11-26-3	94.4	4.05	.463	2.57	296	26	4.31	2.34	1.73	19.5

ing greatly, comparisons between individual curves are facilitated by having nearly equal initial amplitudes. Table II, prepared from the data of Table I, gives equations which have been reduced to similar initial amplitudes. Figure 5, based on the data of Table II, illustrates the difference which temperature and humidity make. For example, increased humidity increases the damping (because there is more viscous flow in the presence of moisture).

2. The results of energy-loss calculations are more quantitative. Observed values for the amplitude of vibration are chosen, and from these the actual ΔE is calculated by using the expression

$$\Delta E = 2\pi^2\nu^2 m(A_0^2 - A_1^2), \qquad (18)$$

where ΔE = energy loss over one cycle, A_0 = amplitude at beginning of cycle, and A_1 = amplitude at end of cycle. Equation (17) gives the theoretical value of ΔE in terms of known constants, the quantities $\Delta F_k^\ddagger$, V_k, and V_m, and the experimental variable A, the amplitude of vibration.

$\Delta F_k^\ddagger$ and V_m cannot be separated, but V_m can be determined from creep data, and there is reason to suppose that it does not vary greatly in different experiments. If a reasonable value is chosen for V_m, two parameters, V_k and $\Delta F_k^\ddagger$, remain. Two points on the experimental curve for ΔE are therefore sufficient to determine these, and the agreement between theory and experiment for the rest

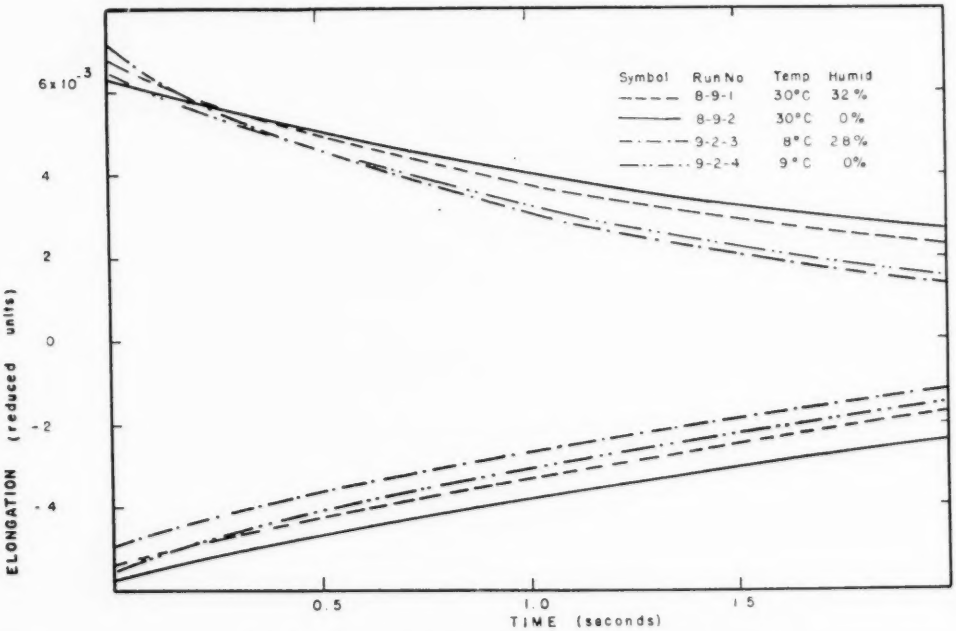


FIG. 5. *Theoretical damping curves, reduced equations.*

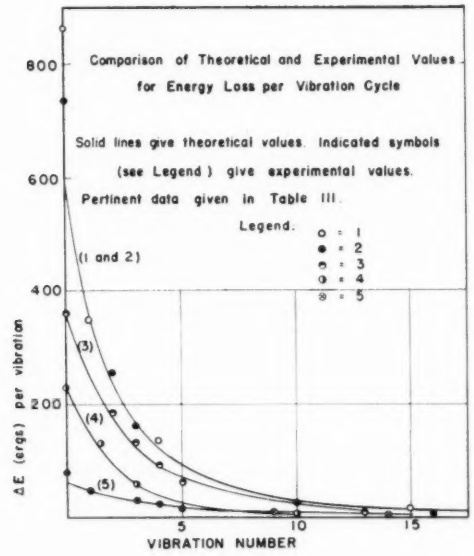


FIG. 6.

of the curve is a measure of the accuracy of the theory. Figure 6 shows that the agreement is good except at the very beginning of the run. This discrepancy is probably due to a transient phenomenon connected with creep in the stretched fiber before vibration starts. Table III presents the data pertinent to the curves in Figure 6. $\Delta F^{\ddagger}$ is seen to be independent of humidity, and to vary with the temperature.

It is particularly significant that the values of $\Delta F^{\ddagger}$ are well below those usually observed in fiber experiments. This is not surprising since the relaxation time is too short (averaging less than 0.2 second) to allow the influence of the higher value of $\Delta F^{\ddagger}$ to be observed as they are in creep experiments, for example.

It would be of the utmost interest to run similar experiments with wide variations in the frequency of vibration. This should lead to the evaluation of a whole range of flow units and reveal basic details of the molecular composition. In order to do this, it would be necessary to turn to forced vibrations, because the range of natural frequencies of any fiber is very limited. Experiments of this nature are now being planned, using a recording strain gage and a motor-driven eccentric as a source of vibrations.

Conclusions

1. A method has been developed for mathematical treatment of a sinusoidal rate of loading of fibers, based on visco-elastic behavior.

2. An experimental technique is described for obtaining data under such conditions.

3. Values have been obtained for $\Delta F^{\ddagger}$ and V_k for the flow process at the natural vibration frequency of the fiber. These values are less than those obtained from creep data, and indicate the need for extending the present investigation over a wide range of frequencies.

Acknowledgments

The authors are grateful to Mr. G. S. Horsley for his assistance in performing the experiments and in the tedious work of analyzing the photographic films. They also appreciate the kindness of the E. I. du Pont de Nemours and Company, Pioneering Research Laboratory, for furnishing the samples used.

Literature Cited

1. Halsey, George, White, Howard, Jr., and Eyring, Henry, Mechanical Properties of Textiles, I, TEXTILE RESEARCH JOURNAL **15**, 295 (Sept. 1945).

2. Eyring, Halsey, *et al.*, Papers II through XI of the above series: TEXTILE RESEARCH JOURNAL **15**, 451 (1945); **16**, 13, 53, 124, 201, 329, 335, 378, 382, 635 (1946).

3. Tobolsky, A., and Eyring, H., Mechanical Properties of Polymeric Materials, *J. Chem. Phys.* **11**, 125 (1943).

4. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill Book Company, 1941, chap. IX.

(*Manuscript received June 27, 1949.*)

INDUSTRIAL SECTION

The Structure of the Wool Fiber

Giles E. Hopkins*

MORE KNOWLEDGE of fiber properties is a necessary preliminary to the building of improved textile structures, just as the knowledge of the physical properties and behavior of metals is all-important to the engineer who designs a bridge or a modern skyscraper.

Accordingly, wool research is, at present, heavily focused on the basic chemical and physical structure of the fiber. To facilitate this work a wide variety of new tools and techniques is now available, and laboratories engaged in wool research constantly report new developments. Some of these reports present new concepts suggested by new observations; some present the proof, and possibly the application, of a more completely established theory. These reports are closely followed by the scientists, but so far they have seldom received the direct attention of the men who must apply them—the mill engineer and the mill executive.

In view of this, the following presentation has been prepared particularly for mill men. We hope that it will serve as an outline map into which subsequent disclosures may be fitted as they occur. In addition, we have touched on the general scheme of investigation of fiber structures now being followed.

We have learned considerable about the physical structure of the wool fiber. We know that the outside surface, or cuticle, is made up of scales which form a sheath or skin around the inner structure—the corticle. We know that the corticle cells are fibrous in nature and are made up of tiny fibrils. Generally, the corticle cells lie parallel to the axis of the fiber and vary from 80 to 110 microns† in length, from 2 to 5 microns in width, and from 1.2 to 1.6 microns in thickness. (A fine, super-merino fiber is from 10 to 30 microns in diameter, whereas a fine, medium wool is from 10 to 40 microns in diameter.) The fibrils are imbedded in an adhesive material and frequently there is, in the center of the fiber, a core of material called the "medulla," which has a honeycomb-like structure built up of many cells of various shapes. (See Figure 1.)

The surface characteristics control the friction between fibers, and the friction, in turn, influences the strength of yarns made by twisting the fibers together. The decrease in the dimensions of a fabric as it is mechanically worked in the wet state is due to the tendency of each fiber to travel through the structure in the direction of its root. Such migration can continue until the fibers are so firmly interlocked that they form a dense felt.

The cuticle scales take up the initial wear on fibers. There may be a thin film or skin on the surface of the scales. At least there is some evidence that abrasion removes a material made up of molecules considerably smaller than the wool molecule, and the existence of such a skin would explain the hollow sacs which appear on the fiber surface when wool is treated with chlorine water.

The high resilience of the wool fiber sets it apart from other fibers. The resilience patterns, the hand, and the chemical activity of wool may vary according to the molecular structure of the fiber. We know that the weathered tips take dye differently from and are harsher to the hand than the unweathered portion of the same fiber. In black or brown wool, variations of color may occur in the same fiber in conformity with changes in the animal's conditions of diet. So important is the effect of nutrition on fiber quality that the condition of the teeth, and hence the ability to obtain nourishment, is a common basis for culling sheep.

* Technical Director, the Wool Bureau, 16 West 46 Street, New York 19, N. Y.

† One inch equals approximately 25,000 microns.

Our knowledge of the actual chemical structure of wool is fragmentary. Twenty years ago we were content to accept an analysis of wool based on the proportions of the chemical elements present. It was reported that wool contained five elements in approximately the following percentages:

Carbon	50%
Oxygen	22%–25%
Nitrogen	16%–17%
Hydrogen	7%
Sulfur	3%–4%

We could guess at the molecular structure of an inorganic compound from such an analysis, because in inorganic chemistry various elements combine according to a few simple patterns. In organic chemistry, however, the same group and even the same proportional distribution of elements can, in some cases, combine in hundreds of thousands of different patterns, and the characteristics of these patterns and the manner in which the different elements lie in relation to each other in these patterns can make tremendous differences in the physical and chemical behavior of the compounds. For example, many parts of an animal are made up of these same five elements in about the same proportions, yet they can be combined to form such different structures as hair, skin, horns, and fingernails.

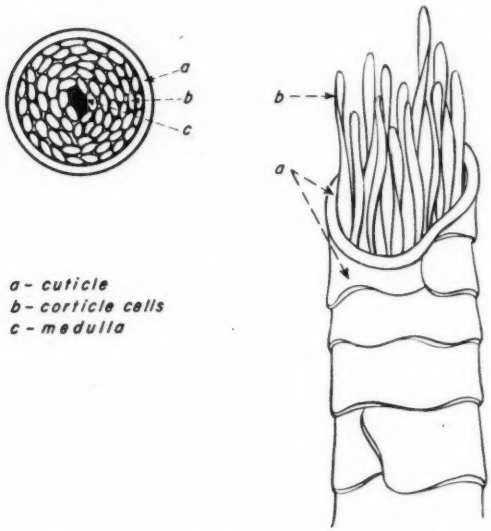


FIG. 1. *Physical structure of the wool fiber.*

We can too easily overlook the fact that a worsted suit is made of the hair of an animal which is grown by the same life processes as all other living structures. Hair is a protein structure. Unlike some of the more simple compounds, proteins break down into sections rather than into individual elements, and each section has complex chemical patterns of its own. It is as though a wrecked train became uncoupled into dining cars, sleeping cars, and coaches instead of shattering into glass, steel, and fabric.

The simplest arrangements of the elements present in the protein molecule, and into which the molecule can be broken down, are the amino acids. More than 20 different amino acids are presently identifiable, and they can be formed into thousands of different combinations. They are grouped together and arranged to form such simple proteins as insulin, pepsin, digestive enzymes, hormones, albumin, and fibrinogen. They combine with pigments to make blood hemoglobin, with complicated sugar structures to form saliva, and with nucleic acids to form nucleoproteins, which are really gigantic molecules. (Genes and viruses are nucleoproteins.)

The amino acids can link themselves together in long chains by chemical combinations. The long chains of amino acids in proteins are called polypeptides. Antibodies, which help us fight disease, are considered to be polypeptides. Countless numbers of these structures are constantly floating in the blood stream. When they come upon some types of bacteria or viruses they are attracted to them. The ends of the chain fold around the foreign substance until they envelop it, rendering it harmless. These polypeptides, floating in the blood, are not rigidly held but are quite free to adapt their folds and configurations to the attractive forces between them and foreign materials.

If the polypeptide chains in wool fiber were as loosely held together as those floating in the blood, the fiber would have no stable shape or ability to recover its original shape after deformation. It would be a weak jelly or liquid. The shape of the wool fiber and its ability to recover after deformation are determined by the nature of certain bonds which hold together the peptide chains in partially stable patterns or arrangements.

Keratin, the protein of the skin, nails, horns, and

hair, is chemically different from the other proteins because it contains cystine. Cystine is important in influencing the behavior of keratin because it has cystine linkages—pairs of sulfur atoms held together by mutual attraction. This bond between the sulfur atoms can be broken or changed or modified with relative ease as compared with, for example, the bonds between the amino acids in the polypeptide chains.

The polypeptide chains are also held together by hydrogen bonds, which are less stable bonds, and certain electrical forces called van der Waals' forces, which are even weaker. The polypeptide chains are folded back on themselves and some of these folds are held in position by hydrogen bonds and the van der Waals' forces. (See Figure 2.)

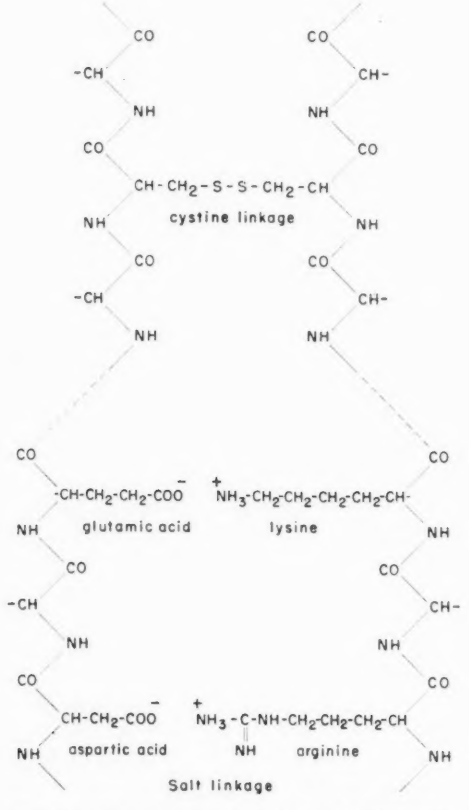


FIG. 2. *Structural formula of wool (Astbury and Speakman).*

But these bonds are not entirely stable and rigid. Although the bonds which connect the peptide chains are sufficiently strong to give the wool fiber a shape of its own; moderate tensions will cause deformation of the fiber.

As the fiber stretches, some of the folds of the peptide chains are straightened and there is slippage between chains. We presume that this deformation is the result of overcoming the van der Waals' forces, breaking of the hydrogen bonds, and modification of the disulfide linkages. If the tension is immediately removed, these forces cause the fiber to approach its original form at once. If we hold the fiber under tension or stretch it beyond its elastic limit, new bonds may be formed in the new position to replace the broken bonds. Then, when the reactive forces of the original, more permanent bonds finally come into play, they must actually oppose the re-formed bonds. "Recovery" is, therefore, slow or never fully accomplished. When the polypeptide chain is in the normal unstretched or folded form it is called alpha (α) keratin. When it is in the unfolded position it is called beta (β) keratin. (See Figure 3.)

The description above and Figures 2 and 3 give a general picture of the chemical structure of the wool fiber. The arrangement of chemical groups and elements is probably different in the corticle cells, in the adhesive substance between them, and in the scales. The important differences may lie in the degree of orderliness of the molecular arrangement, the corticle cells having a more orderly pattern.

It can be seen that the various molecular arrangements in the structure have a direct influence on the

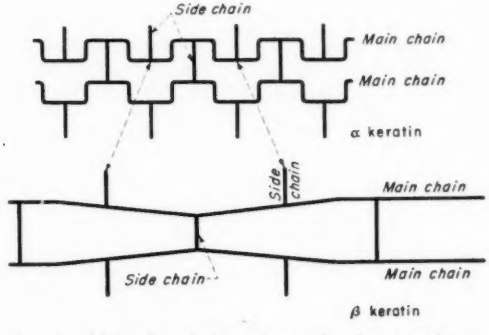
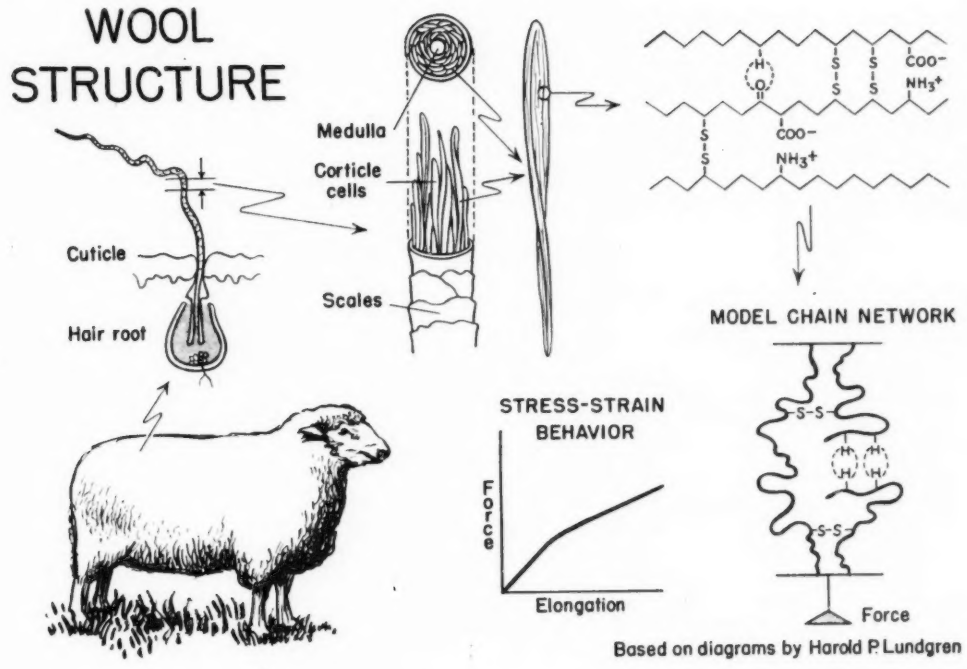


FIG. 3. *Molecular chain patterns showing transformation of α-keratin to β-keratin on stretching.*



way the fiber stretches and recovers from stretch. The patterns which control deformation have a direct influence on the softness of wool to the hand, on maintaining tightness of twist (hence the strength of the yarn), on the ability of a garment to adjust itself to the curves of the body, on the crush-resistance of wool fabrics, on the warmth of a lightweight blanket, and on the relaxation factor in wool fabric shrinkage. It also affects the "set" of wool fibers and of human hair.

Pressing trousers or curling the hair is accomplished by setting the fiber in a deformed pattern by the use of heat and moisture. The set comes out as soon as the fiber is rewet.

The nature of the semi-permanent strains produced in wool fibers during manufacture is less completely understood. The fiber is strained in carding, gilling, combing, drafting, and spinning. Some mills attempt to release these strains by allowing the fiber to "rest" or relax at various stages of manufacture. The ideal conditions for such relaxation are not known.

Our knowledge of the cystine linkage has already been put to practical use in the recently developed cold permanent waves for the hair. In this treatment permanent deformation of the hair in desired patterns is produced by breaking the disulfide linkages which would tend to bring about a return to the original form and chemically replacing these linkages by more stable linkages in new positions.

The disulfide linkage of the cystine bond is easily attacked by mild alkalies and by oxidizing and reducing agents. Wool is exposed to these reagents in many manufacturing processes, in washing with soap and mild alkalies, and in stripping colors. Stable cross-linkages may be substituted which will not be attacked by alkali or oxidizing agents. A commercial process has been developed to do this during stripping, thus combining the protective treatment and the stripping into one operation.

Much of our current investigation of fiber structures resembles an investigation of a Christmas package that we have been forbidden to open. We feel of it and note its shape. We shake it and listen

for a gurgle or a rattle. If we are desperate, we might even drop it sharply to see if the sound changes in character, or we might probe through the wrapping to locate hidden surfaces and, by exploration, actually ascertain their contours.

In studying the chemical structure of the wool fiber we follow the same principle, but we must use much more complex equipment. It is like applying such new developments as the Geiger counter to the investigation of the Christmas package.

We may expose the fiber, or the ground particles of the fiber, to infrared radiation and study the effect of the molecular structure on the intensity of the energy applied. This would give us information about the nature of the bonds and the positions of certain groups of elements with respect to other groups. We may bombard the fiber with x-rays and obtain the deflected patterns caused by the wool molecules, thus obtaining information on the length of the peptide chains, their positions, and the orderliness of their distribution. We may use the electron microscope to study minute changes in the fiber surface after it is subjected to mechanical or chemical treatments.

Since there are several types of bonds holding the peptide chains together, we may simplify our studies by intentionally breaking some of these bonds in order to determine the independent effect of the others. For example, when wool fiber is immersed in concentrated solutions of weak acids, the fiber swells. In this swelling, the peptide chains are moved apart sufficiently to break some of the bonds. Stress-strain diagrams for the swelled fiber show the independent influence of the remaining bonds. Similarly, the fiber may be treated with chemicals to destroy other bonds or to replace them with more stable ones.

Stress-strain diagrams can be obtained in a variety of ways. One method is stretching the fiber and holding it for a considerable period while the change in recovery force is continuously measured. In other methods sudden stresses are applied and the elongation and recovery measured and compared with those which result from more gradually applied loads. Or long series of repeated loads may be applied in rapid succession, even at a speed as great as the speed of sound, and the associated stretch and recovery characteristics noted.

From all of this exploration we can obtain information on the positions of the chains of the amino acids present, the nature of the linkages, the manner in which they are broken and re-formed, and the way in which the long peptide chains unfold. We can obtain information on the chemical characteristics of the various bonds, possible changes in these characteristics, and associated changes in fiber resiliency.

We can also compare the stress-strain behavior of different wools of the same diameter and appearance but of different performance. Correlation of these behavior patterns with associated molecular structure would show the effect of changes in the structure and suggest possible modifications which may be artificially accomplished to provide new characteristics.

From work with much simpler structures, the physical chemists have developed mathematical formulas which express the influence of various formations and characteristics of the molecular structure in terms of associated physical behavior. From these basic formulas it is possible to set up theoretical combinations from which the behavior of more complex formations can be calculated. It is therefore possible to check the validity of an hypothesis by means of comparisons between the calculated performance which might be expected and the actual performance as measured.

And so we have a whole bag of tricks to apply in discovering more about what is in our "Christmas package" of wool fiber; additional knowledge for utilizing, even more effectively, the most useful qualities of this complex fiber structure.

Bibliography

1. Beadle, G. W., The Genes of Men and Molds, *Sci. American* **179**, 30 (Sept. 1949).
2. Bohm, L., Wool Fibres: Frictional Properties in Relation to Felting, *J. Text. Inst.* **37**, A55 (1946). Abst. from *J. Soc. Dyers and Colourists* **61**, 278–83 (1945).
3. Brown, A. E., and Harris, M., Chemical Modification of Wool-Replacement of Disulfide Groups by More Stable Linkages, *Ind. Eng. Chem.* **40**, 316 (1948).
4. Buck, G. S., Jr., and McCord, F. A., Crease-Resistance and Cotton, TEXTILE RESEARCH JOURNAL **19**, 216 (1949).
5. Geiger, W. B., Wool: Scale Structure, *J. Text. Inst.* **35**, A281 (1944). Abst. from *Am. Dyestuff Reptr.* **33**, 117–18 (1944).
6. Gray, G. W., Pauling and Beadle, *Sci. Ameri an* **180**, 16 (May 1949).
7. Hind, J. R., and Speakman, J. B., Optimum Condi-

tions for Setting Strained Animal Fibres, *J. Text. Inst.* **36**, T19 (1945).

8. Hock, C. W., Ramsey, R. C., and Harris, M., Microscopic Structure of the Wool Fiber, Research Paper RP142, U. S. Dept. of Commerce, Natl. Bur. of Standards, Aug., 1941.
9. Lipson, M., and Howard, P., Keratin Surfaces: Friction as Affected by Some Shrinkproofing Treatments, *J. Text. Inst.* **37**, A197 (1946). Abst. from *J. Soc. Dyers and Colourists* **62**, 29–32 (1946).
10. Martin, A. J. P., Wool Felting: Theory, *J. Text. Inst.* **36**, A112 (1945). Abst. from *J. Soc. Dyers and Colourists* **60**, 325–8 (1944).
11. Mercer, E. H., Wool Fibres: Frictional Properties, *J. Text. Inst.* **36**, A346 (1945). Abst. from *Nature* **155**, 573–4 (1945).
12. Mercer, E. H., and Rees, A. L. G., Wool: Structure of Cuticle, *J. Text. Inst.* **37**, A282 (1946). Abst. from *Nature* **157**, 589–90 (1946).
13. Nutting, G. C., Halwer, M., Copley, M. J., and Senti, F. R., Relationship Between Molecular Configuration and Tensile Properties of Protein Fibers, TEXTILE RESEARCH JOURNAL **16**, 599–608 (1946).
14. Peters, L., and Speakman, J. B., The Visco-Elastic Properties of Wool Fibers, TEXTILE RESEARCH JOURNAL **18**, 511–18 (1948).
15. Speakman, J. B., Chamberlain, N. H., and Menkart, J., The Lepedometer—An Instrument for Measuring the Scaliness of Animal Fibers, *J. Text. Inst.* **36**, T91 (1945).
16. Swerdlow, M., and Seeman, G. S., A Method for the Electron Microscopy of Wool, TEXTILE RESEARCH JOURNAL **18**, 536–50 (1948).
17. Thomson, H. M. S., and Speakman, J. B., Wool: Frictional Properties, *J. Text. Inst.* **37**, A410 (1946).
18. von Bergen, W., and Mauersberger, H. R., "American Wool Handbook," 2nd Ed., New York, Textile Book Publishers, Inc., 1948, p. 177.
19. Whewell, C. S., Rigelhaupt, L., and Selim, A., Wool Fabrics: Mechanism of Milling Shrinkage, *J. Text. Inst.* **36**, A112 (1945). Abst. from *Nature* **154**, 772 (1944).
20. Wilson, J. A., "The Chemistry of Leather Manufacture," Vol. I, Chemical Catalogue Monograph, Series No. 12, 1928.

(*Manuscript received October 17, 1949.*)

Direct Steam-Injection Continuous Starch-Cooker

L. W. Rainard* and G. Zanolli†

Alexander Smith & Sons Carpet Company, Research and Development Division, Chemical & Products Research Section, Yonkers, New York

Abstract

A number of different continuous starch-cooking devices are available for the production of starch-based textile pastes and sizes. This paper discusses the advantages and operation of a simple, direct steam-injection type made from standard piping. Characteristics of pastes produced with this type of cooker are also discussed.

THE TEXTILE INDUSTRY as a whole uses extremely large tonnages of starch-based pastes for its sizing and coating operations. Most of the pastes are now produced by a batch process, despite the fact that there are available on the market and described in the literature a number of devices and systems for the continuous production of starch pastes. In many operations, the batch process must, of necessity, be used because of either small requirements or intermittent demand. However, in many cases, the demand for starch paste is continuous and very often great—as much as 500 to 1,000 gals. per hr.

In many textile operations, continuous starch production, with its attendant flexibility and fast production rate, preciseness of control, and potential starch savings, offers decided advantages over the batch system.

Whereas this paper takes cognizance of the fact that there are different types of apparatus for continuous production (the thin-film heat exchanger manufactured by the Girdler Corporation, Votator Division, the mechanical-heating type patented by Caesar and Thompson [1] involving flow through a restricted orifice, and the direct-injection type using either steam or hot water as patented by Coppock [2] and Payne [3]), it will deal only with the direct steam-injection type because of the fundamental simplicity and economy of the equipment and the process. At present, the Schutte-Koerting Company manufactures a small unit suitable for direct-injection steam-cooking. However, it is quite possible to construct an adequate continuous cooker from standard piping.

A direct steam-injection type of cooker was constructed in this laboratory. The equipment used is shown schematically in Figure 1 and in the photograph, Figure 2. It consists of a starch system for raw slurry which contains all of the ingredients combined in the final size and a cooking chamber (Figure 3) into which is fed the raw slurry. A constant-feed pump, such as the gear pump in any of its modifications, capable of withstanding the abrasive action of compounded starch systems, is used to feed the raw slurry to the cooking chamber. The cooking chamber consists of a 2-in.-diameter pipe, 1 ft. long. Steam was introduced into the chamber by means of a multiple inlet distributor consisting of a

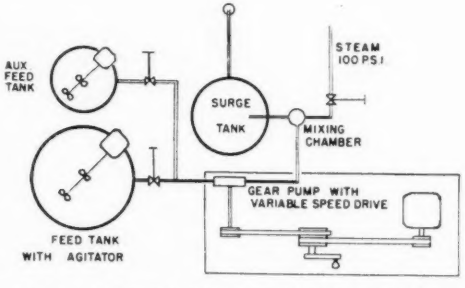


FIG. 1. *Schematic diagram of continuous-cooking system.*

* Chief, Chemical & Products Research Section, Research and Development Division, Alexander Smith & Sons Carpet Company.

† Assistant Chemical Engineer, Chemical & Products Research Section, Research and Development Division, Alexander Smith & Sons Carpet Company.

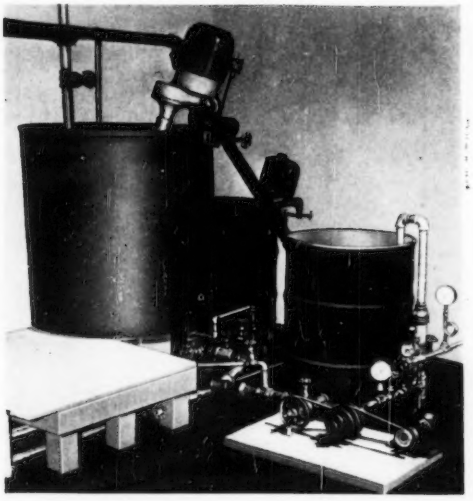


FIG. 2. *Continuous cooking system.*

capped 2-in. section of $\frac{1}{2}$-in.-diameter pipe perforated with ten $\frac{3}{32}$-in. holes. It was found in tests with a smaller cooker that such a type of inlet gave more efficient cooking than one single large inlet. This is indicated in Table I, which presents viscosity data obtained with this smaller cooker using both single and multiple steam entries.

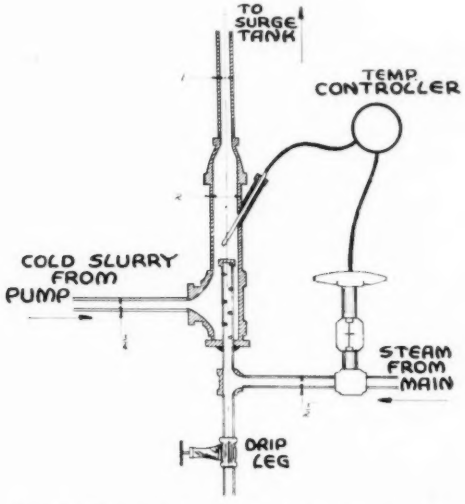


FIG. 3. *Detailed sketch of cooking chamber with automatic temperature control.*

TABLE I. EFFECT OF STEAM INLET TYPE ON THE VISCOSITY OF A STARCH-BASED SIZE COOKED WITH A DIRECT STEAM-INJECTION TYPE OF CONTINUOUS COOKER

Type of inlet	Viscosity* of size† in cp. (Brookfield) at 75°C
Single	1,350–1,850
Multiple	2,000–2,200

* Viscosity of these and all other samples mentioned in this paper measured with Brookfield Viscometer, rotation speed 20 r.p.m.

† Size consisted of starch, filler, binder, extender, and color; starch content, 4%, cooking temperature, 95°C.

For the pilot trials involving the continuous cooker, a system was used wherein there were two storage tanks of raw slurry; while one was in use, a batch was being made in the second. In large-scale commercial operation, the storage tanks are not equivalent in size. One large-size tank takes care of a normal period of operation, which may be an arbitrary period such as 5 days. A small holding tank for raw slurry allows sufficient time for remixing of the large batch. In the pilot trials, 4 days' continuous production was carried out, in which time approximately 3,000 gals. of size were prepared and applied to 150,000 sq. ft. of carpet. A constant flow rate of 1.7 ± 0.1 gals. per min. was maintained during the course of the run. Steam flow was adjusted to give a cooking temperature of $82°C \pm 2$. For this operation, the cooked size was allowed to flow into a surge tank prior to sending it to the size equipment. This was done in order to take up small differences in demand at the sizing machine. Although this cooker was used to feed only one side of the machine, the 2-in.-diameter pipe had sufficient capacity to handle size production rates approximately four times the rate at which this batch was produced.

The simplicity of the setup allows for quick and easy control of cooking temperature, variations in cooking rate, and even intermittent production. With the use of pressure-sensitive relays, the equipment can be made to operate automatically by closing or opening the outlet valve. Temperature regulation is accomplished by the simplest of temperature-regulating equipment since response is practically instantaneous (there may be a very small lag between variation in load or heat supply and the temperature of the mix in the cooking chamber). In our experiments, we did not attempt to develop automatic equipment for varying demand rates.

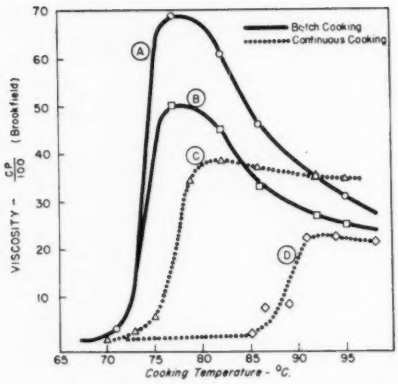


FIG. 4. *Effect of cooking method on the viscosities of starch-based pastes.*

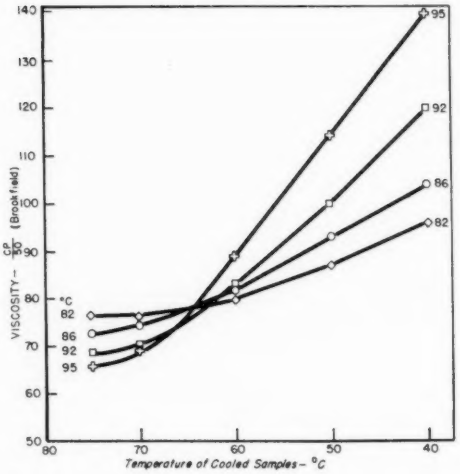


FIG. 5. *Variation of viscosity with temperature for swelled starch-based pastes cooked at different temperatures.*

However, it is possible to develop a simple variable-speed system in conjunction with automatic temperature control which will give smoothly-varying output rates from zero to the maximum capacity of the equipment. The storage system for the raw slurry has to be carefully constructed in order to prevent settling of starch, clay, or other heavy matter in both pipe lines and valves, and the slurry must be slowly agitated during the period of storage in order to prevent settling and to maintain a uniform composition. If raw slurry is to be stored for any length of time without use, provision must be made for adequate reagitation in order to produce uniform feed stock.

The properties of starch pastes produced by the continuous system are essentially the same as those of pastes produced by the batch system. Because the injection steam cooker operates by very rapid heating of differential volumes of starch slurry up to the gelation temperatures, the number of unswollen particles is small, with very short time exposure, in the cooking zone. In a batch process at temperatures at or above the gelling temperature, a large amount of mechanical breakdown occurs because of agitation effects on swollen particles while the remainder of the starch is heated. As a result, the final viscosity of the

TABLE II. EFFECT OF COOKING METHOD ON THE VISCOSITIES OF STARCH-BASED PASTES*

Batch cooking			Continuous cooking		
	Viscosity in cp. (Brookfield) at 70°C			Viscosity in cp. (Brookfield) at 70°C	
Cooking temp. (°C)	Batch A	Batch B	Cooking temp. (°C)	Batch C	Batch D
71	—	300	70	100	—
77	5,000	6,900	73	250	—
82	4,500	6,100	75	550	—
86	3,300	4,600	79	3,300	—
92	2,700	3,500	82	3,830	—
95	2,500	3,100	85	—	190
			86	3,700	—
			86.5	—	700
			89	—	780
			91	—	2,240
			92	3,500	—
			94	—	2,200
			95	3,450	—
			98	—	2,160

* Starch contents of pastes were 3% to 6%.

TABLE III. VARIATION OF VISCOSITY WITH TEMPERATURE FOR SWELLED STARCH-BASED PASTES* COOKED AT DIFFERENT TEMPERATURES

Cooking temp. (°C)	Viscosity in cp. (Brookfield) for samples cooled down to: 75°C	70°C	60°C	50°C	40°C
81	3,830	3,830	4,000	4,350	4,800
86	3,630	3,700	4,100	4,650	5,200
92	3,430	3,500	4,150	5,000	6,000
95	3,300	3,450	4,430	5,700	7,000

* Starch content of paste was 5%.

TABLE IV. EFFECT OF AGITATION* ON THE VISCOSITY OF STARCH-BASED PASTES COOKED AT DIFFERENT TEMPERATURES

Cooking temp. (°C)	Viscosity in cp. (Brookfield) at 61°C for agitation times (min.) of:																
	0	1	4	5	6	10	11	14	15	17	19	20	22	25	26	30	37
95	3,230	1,950	830	—	—	—	550	—	—	—	—	—	430	—	—	—	—
95	3,550	1,630	800	—	—	500	—	—	—	—	—	450	—	—	—	—	—
95	4,100	2,000	800	—	—	630	—	—	—	—	430	—	—	—	—	—	—
85	2,900	2,750	—	1,650	—	1,130	—	—	1,000	—	—	—	—	900	—	980	—
85	3,130	2,880	—	1,700	—	1,150	—	—	—	930	—	—	—	—	830	—	—
79	2,630	2,580	—	—	1,930	—	—	1,400	—	—	—	—	—	1,080	—	—	980

* Samples agitated with single-blade propeller stirrer at 1,700 r.p.m. in 600-cc. beakers. Temperature was maintained at 61°C with constant-temperature bath. Starch content of paste was 5%.

material batch-cooked at temperatures higher than the minimum gelation temperature tends to be lower that that produced by size cooked continuously. Figure 4 and Table II illustrate the relative effects of continuous cooking and batch cooking on the viscosity of samples of starch pastes cooked at different gelation temperatures. It is observed that the viscosity *vs.* cooking-temperature curves indicate a rather narrow temperature range wherein gelation occurs. Once the minimum gelation temperature is reached in the continuous cooker, further increases in temperature of cooking have little effect on the viscosity of the paste. However, if samples of the pastes cooked at various temperatures higher than the minimum gelation temperature are allowed to cool, the final viscosities obtained vary considerably. This is shown in Figure 5 and Table III. Although the lowest cooking temperature gives the highest viscosity measured at the temperature of cooking, it gives the lowest viscosity if the sample is cooled down to temperatures below the minimum gelation temperature.

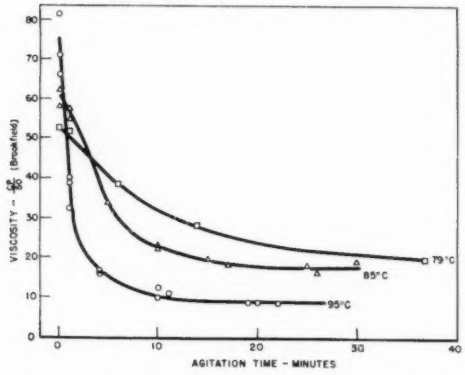


FIG. 6. *Effect of agitation on the viscosities of starch-based pastes cooked at different temperatures.*

Cooking temperatures higher than the minimum gelation temperature tend to produce products which are more susceptible to mechanical breakdown. This is illustrated in Figure 6 and Table IV, which present data obtained by agitating samples cooked at different temperatures under the same conditions. It is observed that the viscosity of the sample cooked at the highest temperature drops much more sharply than that of the samples cooked at the lower temperatures.

These properties are used in practical application. In applications where little or no work is imposed on the paste and a high-viscosity cold paste is desired, a high cooking temperature is used. When it is desirable to make a paste with as high a mechanical stability as possible, then a low cooking temperature is used.

Summary

A direct steam-injection type of continuous starch-cooker was used in pilot trials to make starch-based pastes for sizing and printing. Tests have shown that this type of equipment made from standard piping is simple and economical to operate and is desirable as a continuous-operation piece of equipment.

Literature Cited

1. U. S. Patent 2,417,969, Caesar, G., and Thompson, T., (to Stein, Hall & Co., Inc.), Mar. 25, 1947.
2. U. S. Patent 2,202,573, Coppock, P., (to Distillers Company, Ltd.), May 28, 1940.
3. U. S. Patent 2,313,574, Payne, C., (to Eastman Kodak), Mar. 9, 1943.

(*Manuscript received July 12, 1949.*)

Selection of a Temperature-Measuring System for Textile Mills

C. W. Bowden, Jr.*

PROBABLY the most important single variable in textile processing is temperature. Not only must it be maintained within narrow limits in wet processing, drying, and finishing operations, but it is also important in air conditioning for the mechanical operations of the industry.

Of the various types of temperature-measuring systems there are two which because of their convenience and utility have become by far the most widely used. These are the pressure-type thermometers and the electrical temperature-measuring systems.

Pressure-Type Thermometers

A pressure-type thermometer (see Figures 1 and 2) is operated by the expansion of a fluid as it is heated. The measuring system comprises a temperature-sensitive bulb, connected to the measuring element by means of a length of capillary tubing, and the measuring element, which is a pressure-sensitive hollow metal spiral similar to that used in a pressure gage.

Any change in the temperature to which the bulb is exposed produces a change in fluid volume and, since the system is closed, a corresponding change in pressure. This pressure difference is transmitted through the capillary tubing to the measuring spiral, which converts the change to a movement of the pen or pointer of the instrument.

The fluid fill of a pressure-type thermometer may be either a liquid and its vapor (Class II), a gas (Class III), or a liquid (Class IV). Each of these has its own advantages and disadvantages.

Vapor-Filled Systems

The pressure change of Class II vapor-filled systems is approximately proportional to the square of the temperature change. Because of this fact, they can be used for measuring narrower temperature spans than Class III or Class IV thermometers.

The square root relationship of pressure to temperature in Class II vapor-filled systems results in an unevenly graduated chart with divisions close together at lower temperatures and further apart as the temperature increases. Such charts have the advantage of providing rather wide temperature ranges with good accuracy and readability in the normal operating zone. Consequently, they are often desirable for control applications; however, some individuals object to the nonuniform scales because they find them difficult to read.

Class II fills are unique since only the temperature of the vapor-liquid interface in the bulb is measured. Thus, hot or cold spots along the tubing do not affect accuracy, and no compensation is needed.

Gas-Filled Systems

Compensation of Class III gas-filled systems for changing ambient conditions is simple. It is accomplished by maintaining a bulb volume at least nine times as great as the tubing volume. This ratio reduces to insignificance the effect of temperature differentials along the tubing. Furthermore, Class III systems are somewhat lower in price than Class IV systems. Hence, they are rather widely used where evenly graduated charts are desired.

Liquid-Filled Systems

Class IV liquid-filled systems employ a mercury fill. They have a high pen torque which minimizes tapping error and permits narrow-span instruments, and they may be used to measure temperatures up to 1000° F, higher than is convenient with other types of fill, which are usually limited to about 600° F.

Compensation of Class IV systems, where the length of capillary tubing is 50 ft. or less, is ac-

* Textile Industry Engineer, Minneapolis-Honeywell Regulator Co., Brown Instruments Division, Philadelphia.

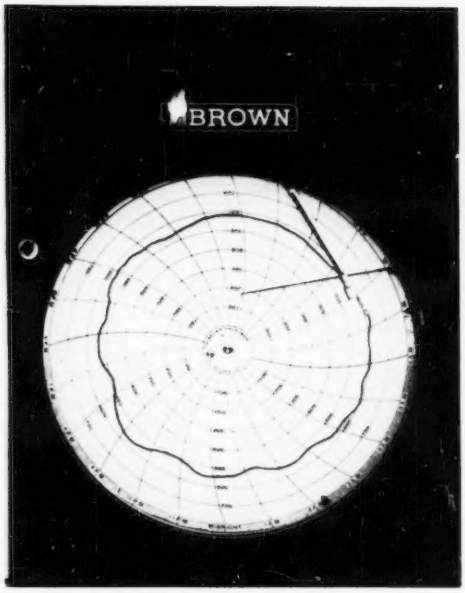


FIG. 1. *The rectangular-case, pressure-type recording thermometer.*

complished by means of a bimetallic strip which adjusts the angular position of the spiral to correct for ambient temperature differential (see Figure 3). When the capillary tubing is more than 50 ft. long, compensation is by means of a parallel line of capillary tubing which terminates close to the bulb and which is connected to a separate compensating spiral.

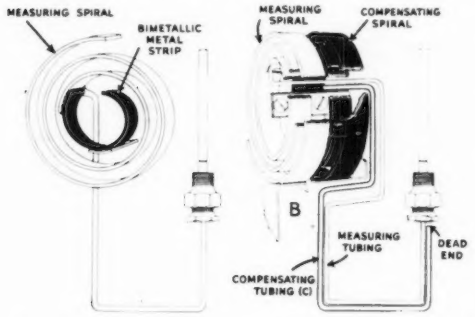


FIG. 3. *Method for compensating mercury-filled thermometers. Bimetallic strip is used for short tubing lengths. The compensating capillary and spiral are used for long tubing lengths.*

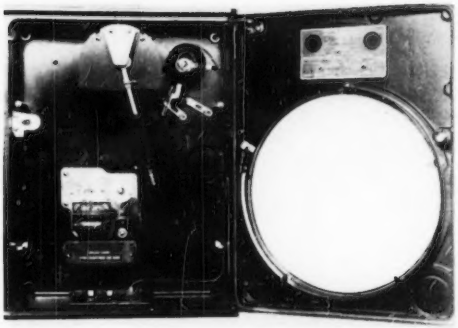


FIG. 2. *Interior of pressure-type thermometer case with chart plate removed to show measuring spiral and linkage to instrument pen.*

This compensating spiral automatically adjusts the measuring spiral to yield the correct temperature reading.

Characteristics of Thermometers

The chief advantages of pressure-type thermometers as a group are their low initial cost and absolute minimum number of moving parts. The cost, however, increases rapidly with greater lengths of capillary tubing. The modern tendency to locate instruments on a remote panel board frequently necessitates long lengths of capillary tubing, with the result that the total installed cost of a thermometer can become as great as or greater than that of an apparently more costly instrument.

The minimum number of moving parts in a thermometer necessitate very little internal maintenance. An occasional calibration check and some attention to the chart drive motor are all that are required for non-control instruments. External maintenance, on the other hand, can become quite a problem. In spite of capillary armor and protection for bulbs, thermal systems do fail. They fail because of mechanical damage, because of vibration, and because of corrosion. Any break in the system allows the fill to escape and necessitates replacement of the entire thermal system. Such replacements are costly and time-consuming. If no spare thermal system is at hand, the thermometer is likely to be out of service for weeks.

Furthermore, it is not often economically sound to stock spare thermal systems. They are expensive

and, because of different capillary lengths and temperature ranges, are seldom interchangeable.

Pneumatic Transmission

Because of the relative costliness of capillary tubing, the sluggishness of response caused by long lengths of capillary, and the possibility of thermal-system failure, it is often desirable to utilize pneumatic transmission, where the measuring point and the instrument must be located some distance apart.

The pneumatic transmission system consists of a transmitter mounted close to the point of measurement, and a receiver mounted at some other convenient location. The transmitter produces an air pressure directly proportional to the measured temperature by means of a flapper and nozzle unit. The air pressure is measured by the receiver, which is essentially a pressure gage calibrated in terms of temperature.

Pneumatic transmission is rapid in response, and can be used for distances up to 1,000 ft. The copper tubing used to transmit the air pressure to the receiver is probably more resistant to mechanical damage than is capillary tubing, and even if the tubing is damaged it can be easily repaired with standard fittings.

Electrical Temperature-Measuring Systems

Electrical systems for measuring temperature may be divided into two broad classes: the resistance circuits and the thermocouple circuits. In general, resistance circuits are used for measuring narrow temperature spans, whereas thermocouple circuits are more widely employed, especially for measuring broader ranges.

Resistance Thermometers

Resistance thermometry is based upon the change in resistance of a metallic conductor as its temperature changes. The sensing element of this system is a resistance bulb, consisting of a coil of small-diameter wire.

Resistance thermometer bulbs possess most of the advantages of thermocouples plus a high degree of accuracy over narrow temperature spans. However, they are more expensive than thermocouples and usually require more protection. The conventional resistance bulb is limited to temperatures below 600° F, but some special bulbs are made for temperatures of 1,000° F.

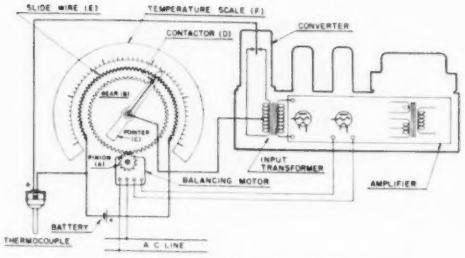


FIG. 4. *Schematic diagram of ElectroniK potentiometer.*

In most cases, the resistance bulb is connected to a self-balancing Wheatstone bridge recorder. Except for the measuring circuit and the fact that no standard cell is needed, this instrument is identical with the self-balancing potentiometers which are described later.

Thermocouple Pyrometers

A thermocouple consists of two wires of dissimilar metals which are welded together at one end. When this welded end (called the *hot junction*) has a temperature which is different from that of the opposite ends of the wires (called the *cold junction*), a small voltage is generated. The magnitude of the voltage is proportional to the temperature difference existing between the ends of the thermocouples. By means of suitable extension wire, the cold junction is extended to the measuring instrument.

Thermocouples are made in a variety of sizes and from several combinations of metals, which permits temperature measurements in practically any desired range. Consequently, it is possible to choose a thermocouple which is well adapted to nearly every temperature-measuring application.

Thermocouples are a very convenient means for temperature measurement because of their high sensitivity, excellent reproducibility, low cost, and convenience of replacement. Furthermore, they are interchangeable, and the extension wire used with them can be easily repaired by splicing in case of breakage.

The ElectroniK Potentiometer

Although thermocouples may be used with deflectional instruments such as millivoltmeters, they are

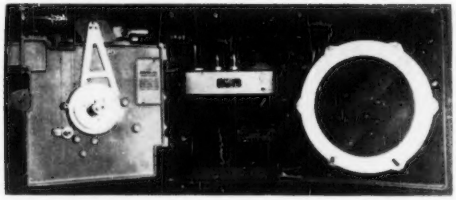


FIG. 5. *Interior view of ElectroniK potentiometer showing that moving parts have been reduced to a minimum.*

far more frequently employed with null balance instruments or potentiometers in the textile industry. In the potentiometer, the e.m.f. from the thermocouple is balanced against a known e.m.f. from a battery. Thus, highly accurate temperature measurements are obtained and the accuracy is maintained continuously.

Formerly, potentiometers were balanced by mechanical means, and a galvanometer was used to detect unbalance. About 10 years ago, Brown pioneered a new principle in self-balancing potentiometers. In this new ElectroniK potentiometer (see diagram, Figure 4) an electronic unit amplifies any electrical unbalance, and the amplified current is employed to drive a reversible motor. The motor rebalances the circuit and also drives the recording pen and pointer.

The most significant advantage of this instrument is that it remains in continuous balance, following every change in temperature as the change occurs (see Figure 5). This is different from the mechanical instrument which rebalances periodically and consequently does not measure a change until an appreciable time has elapsed after the change has occurred.

Because of the simplicity of the ElectroniK potentiometer, it employs a minimum number of moving parts. Furthermore, these few parts operate only when there is a change in the measured variable. As a result, maintenance of this instrument is very inexpensive.

The advantages of the ElectroniK potentiometer for temperature measurement are many. When used with a thermocouple as the temperature-sensing element, it constitutes a rugged, trouble-free system, combining high sensitivity with ample pen power. Neither the sensitivity nor the accuracy of the instrument is affected by external circuit resistance, which makes it possible to locate the indicator or recorder at almost any convenient distance from the point of measurement.

About the only limitation of the potentiometer is its higher initial cost. Even this is relative, however, since there is often little difference between the actual installed cost of a potentiometer and that of a thermometer with a long length of tubing. Maintenance costs may also favor the potentiometer.

Selection of a Temperature-Measuring System

There is no one type of temperature-measuring system which will best satisfy all mill requirements. Each application must be considered separately and analyzed carefully. Some of the more important factors which should influence the final selection are: (1) the range of temperature to be measured; (2) the degree of sensitivity and accuracy needed; (3) the distance between the instrument and the measuring point; and (4) the importance of the measurement to continued production.

Experience has proved that selection of a temperature-measuring system can, in most cases, best be made by cooperation between mill personnel and instrumentation engineers. This combines the experience and know-how of men familiar with both sides of the problem and prevents such errors as may occur because of failure to consider all pertinent points.

The subject of temperature measurement is far larger and more complex than it might seem at first. Obviously, only a few of the high spots can be touched upon in so brief a report as this. It is hoped, however, that the major advantages and limitations of each type of temperature-measuring system have been somewhat clarified.

(Manuscript received August 2, 1949.)

Laboratory Techniques

New Methods* for Holding Multi- and Single-Filament Tensile Specimens

Richard LaTorre and Waller George

Naval Research Laboratory, Washington, D. C.

THE PRECISE EXPERIMENTAL determination of the load-strain relationship for fibers and yarns involves at least three separate problems: (1) the specimen, (2) the testing machine, and (3) the recorder. It is the purpose of this paper to discuss some recent developments concerning the first of these. Although many of the ideas to be discussed are rather straightforward generalizations of testing practices in other fields, it is thought that they represent a somewhat different point of view from that currently in vogue in the textile and fiber testing field, and hence will find some interest among fiber technologists.

The scatter in rupture-strength measurements of a given lot of technical metal such as aluminum is known to be quite small—*i.e.*, $\pm 3\%$. One might ask, then, why it is that comparable strength measurements for textile yarns or single filaments show such a wide scatter. This scatter is particularly noteworthy in the case of synthetic fibers which have been spun and drawn into extremely long lengths without rupture. An attempt has been made by the authors to study statistically the scatter in the results of tensile tests on synthetic yarn of high strength and good physical uniformity using a wide range of gage lengths, according to A.S.T.M. Standards [1, 2]. Without a detailed discussion, it can be stated that the results of this attempt clearly indicate the operation of some mechanical feature which is not statistically distributed within the yarns. Although, in part, the results may be due to twist effects (the yarn used had a low twist—about 1 per in.), it is felt that the primary source of the observed scatter is traceable to the changing load distribution in the twisted yarn during application of load and the resulting elongation of the specimen. It therefore seems reasonable to search for mechanical techniques which can be used to minimize asymmetries in the load distribution which appear during load application.

The technique described below apparently accomplishes the desired redistribution. It is a direct generalization of the standard method used for tensile testing of metals, with one important exception. The difference is that for yarn it is necessary to allow some longitudinal slippage* of the fibers over one another in the region where they are fixed to the testing machine; this region we shall call the "head." A metal accomplishes this load redistribution by certain small plastic rearrangements in the vicinity of the head. These rearrangements are likely to be confined to the immediate region of the grain or crystallite boundaries. It is true that any single filament allows this type of mechanism to operate, but apparently the usual "pressure clamp" or "wrap-around drum" types of fiber support do not allow for sufficient longitudinal readjustment of the various grain-like domains within a fiber so that the elements will each bear a nearly equal portion of the total load. What is required is a somewhat "soft" head which will permit the required load-equalizing motions among the individual filaments in the case of yarn, or internally in the case of a single filament. The internal rearrangement of the load must be accomplished without excessive localized plastic flow and associated stress components which are other than parallel to the fiber axis, applied load, and resulting strain. This requires that the heads be symmetrical about the fiber axis and the direction of load or strain application.

Application of the criteria discussed above has resulted in an experimental design of multi- and single-filament heads. Figure 1 shows a typical single-filament specimen. The specimen is threaded

* Patents pending.

* The use of the term "slippage" refers to a *localized* reorganization of the specimen components relative to themselves and their surroundings, which occurs under load application, in an attempt, on the part of the specimen, to equalize the load distribution among its component parts.

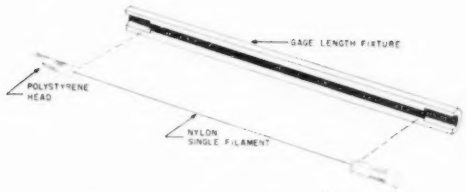


FIG. 1. *Single-filament specimen.*

through a small-diameter hole in a plastic rod of suitable dimensions and composition. The filament is then cemented to the head. The gage length of the specimens can be held constant by employing a fixture which spaces the heads. In one particular application, single-filament specimens of Type 300, 5-den. nylon were cemented to polystyrene heads with Duco cement.

Soft heads for multifilament yarns have also been designed. These are illustrated in Figure 2. The fiber is held inside a hollow metal tube by means of a suitable thermoplastic filler. The tube is threaded on the inside to insure a positive grip on the plastic filler. Both ends of the tube are counterbored to provide seats for stiff, perforated enameled paper inserts which insure the position and alignment of the fiber. After the fiber has been assembled to the tube, it is filled with the plastic by gravity from a reservoir of the molten plastic filler. A small hole on the side of the tube permits trapped air to escape during filling. After the tube has been filled, it is allowed to cool and the head is complete. The same operation is repeated at the other end of the specimen. Cellulose caprate makes an ideal head filler for high-strength Type 311 nylon yarns (5 210/34, 8 g. per den.). To insure uniform gage lengths a fixture is used which maintains the distance between the heads while they are being formed.

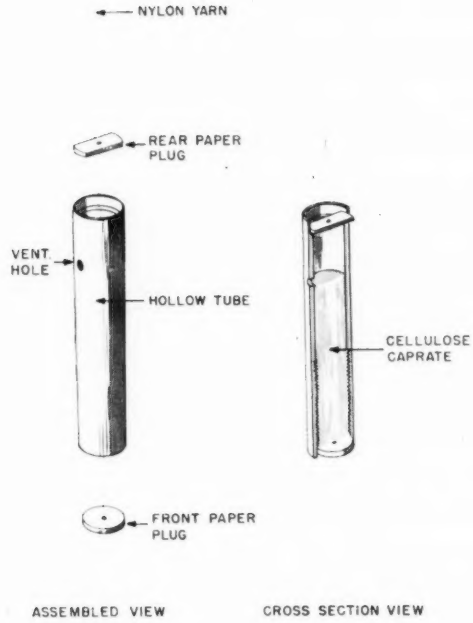


FIG. 2. *Yarn specimen head.*

Figure 3 is a photograph of one end of a multifilament fiber fixed to the carriage of a Scott Model IP-4 inclined-plane testing machine. Collets are used to couple the specimen to the testing machine. The collets are mounted in spherical seats to assure better axial alignment between the heads, the specimen, and the direction of the load application.

Certain preliminary studies of the breaking strengths of both nylon monofilaments and multifilament specimens have been made. For monofilaments the scatter in the breaking strength is of the order of $\pm 2\%$ of the mean strength for small (10–20 individual) test lots. When the breaking strengths of low-twist multifilament yarn specimens obtained with plastic heads are compared with similar measurements obtained using conventional gripping procedures, one notes an appreciable reduction in the scatter of the results over a wide range of gage lengths. Curves of rupture load *vs.* gage length for low-twist, high-strength nylon yarns apparently show significant structure which is completely within the scatter region for data obtained using conventional supporting methods.

During loading, the multifilament plastic-fiber interfaces separate to a small degree in the region of the head. It is felt that this separation (and attendant slippage) results in a process of redistribu-

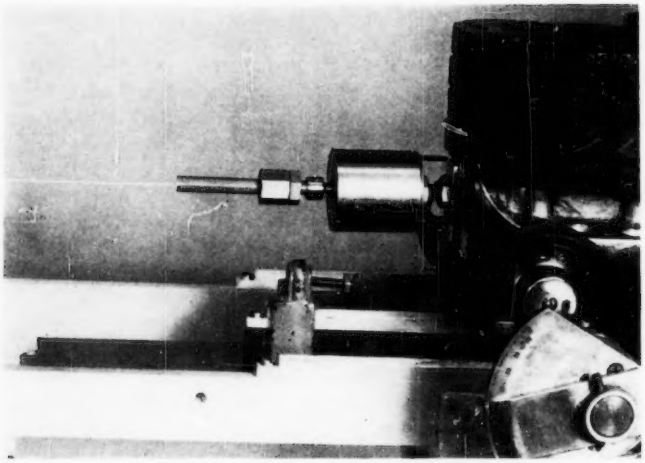


FIG. 3. *Yarn specimen held in Scott IP-4 inclined-plane testing machine.*

tion of the load among the component filaments. The desirable uniformity of load distribution is obtained at the expense of an initially determinate and constant gage length. This uncertainty is negligible for specimens as long as 10 in. but, in the authors' experience, introduces as much as 100% uncertainty

FIG. 4. *Ruptured yarn specimen.*

in the gage length of specimens as short as $\frac{1}{2}$ in. Similar effects exist in the standard "wrap-around drum" type of clamping devices, except when the specimens tested are very brittle. Figure 4 shows a typical ruptured specimen of a high-strength nylon yarn. Note the feathering of the ruptured ends, which is thought to be typical of breaks in uniformly loaded yarns.

In the types of head described above, the total amount of specimen initially (prior to load or strain application) within the head does not remain similarly located throughout the loading epoch. The total motion of one head with respect to the other is composed of the elongation under the applied load of the initial gage length plus an error motion. The latter displacements are, in turn, of two types: (1) the localized head slippage described above, and (2) the natural longitudinal elongation of the material which has "slipped" from within the head, which bears the same macroscopic load supported by the material in the initial gage length.

The authors appreciate the fact that the procedure and technique discussed herein are probably not the best or the most economical from the standpoint of commercial testing of textile materials. However, it is hoped that the discussion has been suggestive with respect to a general approach to the problems of either static, dynamic, or impact testing of textile yarns and fibers. The approach appears particularly attractive for fundamental studies of the mechanical strength of fibers, yarns, and threads.

Literature Cited

1. George, W., and LaTorre, R., *Phys. Rev.* **74**, (A) 1256 (1948).
2. A.S.T.M. Standards, Philadelphia, 1946, Part III–A, pp. 484–8.

(*Manuscript received July 20, 1949.*)

Letters to the Editor

Dry Needle Cooling in Heavy-Duty and High-Speed Machine Sewing Operations

E. I. DU PONT DE NEMOURS AND COMPANY, INC.
Wilmington, Delaware
October 3, 1949

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Many fields of heavy-duty and high-speed machine sewing have been closed to synthetic fibers because needle heating causes some loss in seam strength under continuous-load sewing, and fusing when the sewing run is terminated. Similarly, in natural fibers there is reason to believe that a serious loss of seam strength results from excessive needle heating. With synthetic fibers, increasing thread size usually allows sewing in an operation where fusing is an issue, but nullifies the advantage of obtaining increased seam strength with decreased yarn size.

Some time ago, while attempting to solve the problem of yarn fusing in multiple-needle leather sewing operations, a new needle cooler was devised by one of the authors.* It was based on the principle of cooling in rapidly expanding compressed gas jetted directly onto the needle. The critical points of design were seen to be the shape of the orifice, the direction, velocity, and diffusion of the jet, and the proximity of the orifice to the needle. In practice, the jet of gas may be located either above or below the sewing table, space permitting.

A cooling head (Figure 1) with an opening 0.010 × 0.500 in. was subsequently fabricated and tested at the Carothers Research Laboratory, and later at, and with the cooperation of, the Premier Thread Company, Pawtucket, Rhode Island, under the supervision of a du Pont representative.† When this cooling head, employing 50 p.s.i. plant air controlled by a valve operating in conjunction with the treadle mechanism, was mounted on the foot of a standard Singer No. 107W1 sewing machine within 0.1 in. of the needle, it was possible to sew several thicknesses of "ORLON" * awning fabric with nylon sewing thread continuously and without trouble. Without the needle cooler, the machine could not be brought up to medium speeds even for short runs without consistent thread melting when the run was terminated. Likewise, in single-needle edge-stitching the use of the cooler allowed continuous and or intermittent sewing of all leathers except Scotch grains.

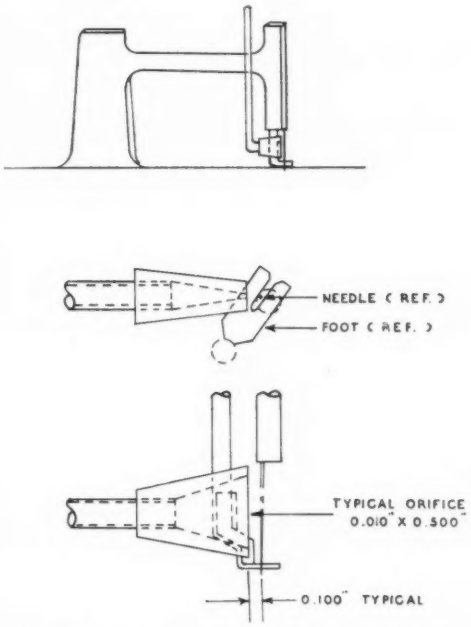


FIG. 1. *Gas cooler for sewing-machine needles.*

* H. F. Hume.
† T. O. Lee.

* Du Pont trademark for its acrylic fiber.

It is believed that the experiments with single-needle applications indicate that proper sewing-machine modification, mounting, and gas delivery would result in successful multineedle operation.

In a further extension of the principle, in those operations where spotting and moisture lubrication of the fabric are less critical, the efficiency of cooling may be increased by introducing continuously a small amount of fluid on the higher-pressure side of the orifice at a rate which will cause breakage of the stream into extremely fine droplets.

H. F. HUME *
T. O. LEE †

* Research Chemist, Carothers Research Laboratory, Rayon Technical Division, E. I. du Pont de Nemours and Company, Inc.

† Technical Investigator, Development Section, Rayon Technical Division, E. I. du Pont de Nemours and Company, Inc. Present address: Premier Thread Company, Pawtucket, Rhode Island.

T.R.J. Index for 1949

THE INDEX to Volume XIX, 1949, will be printed as a separate publication and mailed to subscribers to Volume XIX early in 1950.

Book Reviews

Physics and Chemistry of Cellulose Fibres (with Particular Reference to Rayon). P. H. Hermans. New York, Elsevier Publishing Company, 1949. 534 pages. Price, $9.50.

(Reviewed by John A. Howsmon, American Viscose Corporation, Marcus Hook, Pennsylvania)

Dr. Hermans states that his aim in writing this book "will have been attained if it strengthens the bond between technical science and research and proves an incentive to further research." He seems to have done his part in the attainment of this aim in that his stimulating discussion should arouse the interest of both rayon technologists and fundamental research workers.

The material, which is well organized, is divided into three parts. The first part, entitled "Constitution, Crystallinity, Micellar Structure, Molecular Weight, Chemical Behavior, and Dispersion of Cellulose," deals with the general principles of cellulose materials not directly connected with the specific form of a fiber.

Part II, "General Properties of Cellulose in the Form of Fibres, Morphology and Micro-Structure, Physical and Chemical Behavior of Cellulose Fibres," is a general survey of the physical and chemical characteristics of cellulose in terms of fiber structure. The interpretation is restricted to cellulose alone, but many of the principles can be applied directly to other polymeric systems.

Part III, "Artificial Cellulose Fibres," treats the fundamental principles underlying spinning of fibers from cellulose solutions in relation to the structure and behavior of regenerated cellulose filaments. Many analogies are drawn between the swelling, deformation mechanisms, orientation, and other properties of swollen cellulose gels and other rubber-like materials.

Parts II and III are especially interesting because, in addition to covering a wealth of new data, they fill in many of the gaps in previously existing literature. The author has fearlessly added his own interpretation of many controversial points and has drawn many interesting and informative conclusions. The excellent treatment of these controversial topics, many of which may be subject to revision as new data accumulate, makes this book unique in the field of cellulose research.

The text is accompanied by numerous excellent illustrations, and in spite of the fact that many publications were not available to the author during the war years, the bibliography is extensive. Dr. Hermans' valuable contribution to the literature should find wide use as a reference.

Industrial Rheology and Rheological Structures. Henry Green. New York, John Wiley & Sons, Inc., 1949. 311 + xii pages. Price, $5.50.

(Reviewed by Charles H. Lindsley, American Enka Corporation, Enka, North Carolina)

This book by the late Henry Green presents a system for measurement of rheological properties, developed largely by a small group of investigators associated at one time or another with E. C. Bingham. The book contains much useful material.

In parts I and II, supplemented by appendices, Green presents the mathematical and experimental bases of capillary and rotational viscometers. He shows convincingly the inadequacy of one-point methods to characterize non-Newtonian materials and proves that suitable multi-point methods are neither difficult nor time-consuming. His description of microscopical study of flow in capillaries (in which he was a pioneer) is very helpful in visualizing plastic flow. The discussion of the several types of flow—Newtonian, plastic, pseudoplastic, and dilatant—is in general very satisfactory. (This reviewer takes issue, however, with the statement on p. 77 that at low rates of shear a pseudoplastic material "for all practical purposes behaves like a Newtonian.")

Part III, dealing mainly with determination of particle size, will be useful primarily to those in the paint and ink industries.

The glossary of rheological terms at the end will be found helpful.

The organization of the book is confusing. It was not intended as a textbook (perhaps this explains the absence of chapter headings), yet it has many of the characteristics of one, even to the problems and questions at the end of a third of the chapters. In several parts, and generally in the best parts, it is a practical working manual; for example, it gives details for constructing, calibrating, and operating a rotational viscometer and for examining particle suspensions microscopically. But along with these practical matters are discussions of such recondite subjects as the three coefficients of thixotropic breakdown and Reiner's "rheological systematics." Finally, the author includes personal opinions and whimsical observations on the lot of the industrial rheologist; occasionally, he lapses into an informality that would be pleasant from the lecture platform but seems out of place on the printed page.

The book is marred, unfortunately, by a number of errors. Many of these are of the obvious typographical variety, but there are quite a number in various mathematical equations, and these may give trouble to anyone attempting to work through the derivations for himself. The final equation, in every case, seems correct (though not always in the simplest form); the errors occur in the intermediate steps. Other errors may give the student more trouble. For example, it is stated (p. 12) that when a cross-sectional diagram is made of the velocities of the various layers of flow in a capillary, the pattern for a plastic material is not a truncated parabola; yet Figure 36 shows one truncated, not one with the two halves pushed apart. Again, on p. 67, R is referred to as a function of t, and yet by definition (p. 53) R is simply the proportionality constant between top r.p.m. and the time taken to attain it.

Some parts of the book are difficult to follow, such as Chapter 5 on thixotropic breakdown. Chapter 9 on "tack" is also confusing, partly because the author does not attempt to define this ill-defined property until near the end, and then concludes that tack is not a valuable measurement unless put on a relative basis.

In short, the book stands in need of careful editing to eliminate unessential matter and to clarify many sections, as well as to correct obvious errors. Editing is also needed to eliminate undue repetition, as in the three discussions of dilatancy. Perhaps, had he lived, Mr. Green would have met these criticisms before publication, whereas Miss Weltmann, who took over the task of seeing the book through the press, may not have felt free to make the rather drastic changes needed.

In conclusion, the ore of this book contains enough valuable metal to make it worth extracting. The need for such a book exists, and a good start—the hardest part—has been made. One may hope, however, that someone will undertake the task of editorial beneficiation, to remove much of the dross and to enrich the ore.

Textile Laboratory Manual. Walter Garner. London, England, National Trade Press, Ltd., 1949. 488 pages. Price, 30*s* net.

(Reviewed by Edward A. Murray, Deering Milliken Research Trust)

In view of the diversified subject matter covered in this text, it is a remarkably complete work. Twenty-one chapters cover the following subjects: Wool and Hair Fibers, Vegetable Fibers, Filament Fibers, Quantitative Fiber Analysis, Regain and Relative Humidity, Strength and Stretch Tests, Yarn Properties, Fabric Properties, Insulation, Sizes and Related Materials, Detection of Metals, Color, Evaluation and Analysis of Dyestuffs, Detergents and Wetting Agents, Textile Oils, Water Supplies and Effluents, Textile Chemicals, Biological Methods, Optical Methods, Viscosity Methods and Statistical Methods.

Few typographical errors are apparent, but American readers will readily detect such technical misstatements as "Polystyrene rayon burns like a candle, giving a paraffin smell" and reference to the low flexibility of polyethylene and polyvinyl acetate. In any book including such a wide variety of test methods, it is to be anticipated that a few topics, of relatively great interest in certain laboratories, will not be as thoroughly treated as might be desired. While there are no conspicuous omissions, the chapters dealing with filament fibers, sizing materials, and detergents might profitably have been somewhat enlarged. Although reference is made to the resin treatment of fabrics, this subject has been all but omitted, probably because resin finishes are not yet as widely accepted in England as in this country. The large number of literature citations

throughout the text, a considerable proportion of which are American, will undoubtedly be found particularly valuable.

The chapters on insulation, color, and the evaluation of dyestuffs are well organized and most informative. Because of differences in instruments and techniques between the United States and Great Britain, much of the material dealing with physical testing will be of limited value in so far as direct laboratory application in this country is concerned.

Although this book could not readily be adapted for use in textile-school laboratory courses in this country, it will undoubtedly be found very useful as a reference work. In fact, it was designed primarily as a reference work for those engaged in textile laboratory work and was written with the object of bringing together in one volume a complete range of physical and chemical test methods. This goal has been achieved to a remarkable degree, considering the difficulty of the task.

Monomers, Volume I: A Collection of Data and Procedures on the Basic Materials for the Synthesis of Fibers, Plastics, and Rubbers. Edited by E. R. Blout, W. P. Hohenstein, and H. Mark. New York, Interscience Publishers, Inc., 1949. 368 pages. Price, $7.50.

(Reviewed by G. L. Wesp, Monsanto Chemical Company, Central Research Department, Dayton, Ohio)

This is a loose-leaf collection of planographed pamphlets dealing with the preparation, purification, analysis, handling, physical properties, chemical reactions, and polymerization of eight common monomers, namely: acrylonitrile, butadiene, isobutylene, isoprene, methyl methacrylate, styrene, vinyl acetate, vinyl chloride. Subsequent volumes are to include other vinyl monomers, as well as intermediates for condensation polymerizations.

For a work with so many objectives, all sections are reasonably complete except those covering polymerization. Admittedly, such a compendium as *Monomers* cannot serve as a handbook on polymerization. Moreover, although the editors' objective was to recommend the most effective recipes and techniques, many of the processes described would, if followed, result in slow reactions, poor yields and or inferior products. Some examples of misleading or out-of-date statements are: on page 34, with respect to acrylonitrile, if the suggested procedure were followed, one would be faced with the task of dispersing 856 grams of monomers in 400 ml. of water; the statement on page 29 that polyvinyl chloride cannot be plasticized is false; concerning isoprene, on page 31 the inference that benzoyl peroxide is the most widely used catalyst for the production of synthetic rubber is, at best, out of date, and, within the past 10 years, false; and the statements on pages 7 and 20 contradict each other with respect to the sensitivity of isobutylene to attack by atmospheric oxygen. Moreover, more rigid editing would have caught the numerous typographical and grammatical errors.

For chemists interested in monomer preparation and properties, this publication may serve as a convenient reference. Its utility for other purposes is questionable.

Surface-Active Agents: Their Chemistry and Technology. Anthony M. Schwartz and James W. Perry. New York, Interscience Publishers, Inc., 1949. 579 + xi pages. Price, $10.00.

(Reviewed by Earl K. Fischer, National Bureau of Standards, Washington, D. C.)

In the last two decades the number and variety of surface-active compounds have increased greatly, and their industrial uses have expanded in the same degree. Until this book appeared, there was no monograph that could be considered as describing adequately the chemistry, manufacture, and application of these compounds. The present volume is a valuable if not an indispensable guide in this field.

The authors have arranged their material in the following sections: (1) an introductory discussion, including nomenclature and a system of classification (19 pages); (2) processes for synthesizing and manufacturing (213 pages); (3) physical chemistry of surface-active materials in theory and practice (150 pages); and (4) practical applications (120 pages).

Information on the synthesis of surface-active agents is drawn chiefly from patents. This is al-

ways a difficult and vexing source of information, but the authors have made their digests quite readable. A valuable feature is the identification of chemical structure with trade names.

The section on physical chemistry of surface-active compounds follows the familiar form, but it is useful primarily for the application of theory to practical processes. Considerable material from recent journal articles is summarized. Those familiar with the subject will recall the 1945 conference on surface-active agents held by the New York Academy of Sciences in which an effort was made to correlate theory with empirical measurements and practical uses. This conference showed the need for additional experimentation, for many questions remained unresolved. The present authors, after reviewing the available literature, conclude quite plausibly that "further strides will depend on sounder, more fundamental methods for measuring the gross effects themselves."

For the plant chemist, the section on uses of surface-active materials will be of most interest. Many applications are illustrated, including cosmetics, household preparations, paints, printing inks, pigments, petroleum, ore flotation, building materials, leather, pharmaceutical preparations, and food. The chapter dealing with the textile industry covers 37 pages, and, although many uses are noted only briefly, citations to the literature facilitate further reference.

Extensive author and subject indices add to the reference value of the volume.

This book can be recommended without reservation.

Developments in the Cotton, Rayon, and Silk Industries in Germany During the Period 1939–1945. British Intelligence Objectives Sub-Committee Overall Report No. 13, 1949. 178 pages. Price, $1.00. Available from British Information Services, 30 Rockefeller Plaza, New York.

This report draws on the findings of numerous investigators who have visited Germany since the German surrender and attempts to assess critically the contributions that the Germans have made during this period.

Mechanical processing; bleaching, dyeing, and finishing; research and development; testing methods; and textile education are surveyed and an appendix is included listing trade names and compositions of German textile products. Another appendix lists the targets visited in Germany, with reference in each case to the B.I.O.S. Final Report covering the investigation.

U.S.D.A. Patents. List of Patents with Abstracts, January 1, 1944–June 30, 1949. Single copies of the list are available upon request from Southern Regional Research Laboratory, 2100 Robert E. Lee Boulevard, New Orleans 19, La.

Southern Laboratory patents, assigned to the United States Government, containing information of importance to cotton textile manufacturers, oilseed processors, and a number of other American industries in the South and elsewhere are listed, with abstracts describing the essentials of the process or method covered by each patent.

All of the patents listed are available for license on a royalty-free, non-exclusive basis.

T.R.J. to Start New Plan for Furnishing Abstracts to Subscribers in 1950

In January, 1950, TEXTILE RESEARCH JOURNAL *will begin a new method for handling technical abstracts. By arrangement with the Textile Institute, Manchester, England, the Abstracts section of the* Journal of the Textile Institute *will be bound and mailed monthly to the subscription list of* TEXTILE RESEARCH JOURNAL. *Also at this time the current Abstracts section of* TEXTILE RESEARCH JOURNAL *will be discontinued.*

There will be no extra charge to subscribers to TEXTILE RESEARCH JOURNAL *for the new abstracts service.*

Through this arrangement with the British Textile Institute two purposes will be served: (1) simplification of the present abstract situation, in which the multiplicity of abstract services, most of them limited in scope, is confusing to everyone who desires to keep posted on developments, and (2) a broader coverage of the general literature pertaining to textiles will be furnished to readers of TEXTILE RESEARCH JOURNAL.

The collaboration between the Textile Research Institute and the British Textile Institute represents a constructive effort toward reducing the duplication of abstracts appearing both in TEXTILE RESEARCH JOURNAL *and the* Journal of the Textile Institute.

In as much as the latter carries a good coverage of domestic and foreign publications, in both technology and science, it is believed that subscribers to TEXTILE RESEARCH JOURNAL *who are also receiving the* Journal of the Textile Institute *will be able to make good use of this separate copy of the British Abstracts. Business executives also will find it advantageous to have under separate cover a monthly abstracts publication covering the general developments in textiles.*

ABSTRACTS*

ANALYSIS: TESTING: LABORATORY METHODS

★

Multipurpose Abrasion Tester

An improved multipurpose abrasion tester and its application for the evaluation of the wear resistance of textiles. R. G. Stoll. TEXTILE RESEARCH JOURNAL **19**, 394–415 (July 1949).

On the basis of a systematic consideration of the mechanics of fabric wear and abrasion and extensive experimentation with various test methods and machines, an improved multipurpose abrasion tester has been developed under the research program of the Quartermaster Corps. This work was carried out jointly by the Quartermaster Textile Materials Engineering Laboratory and the Textile Section of the National Bureau of Standards. The apparatus is capable of quantitatively measuring resistance to flat-, edge-, and flex-abrasion under carefully controlled conditions, and producing macro- and micro-wear patterns which are the same as those obtained in actual wear. Materials tested in the machine are abraded to an endpoint which is quantitatively defined and independent of individual judgment. Deviations in test results due to the machine are insignificant compared to the deviation of the samples themselves. A correlation has been found to exist between accelerated combat-wear data and results obtained on the new tester. *Text. Research J. Dec. 1949* Author

Adsorption of Color by Fibers

The adsorption of color on textile fibers. J. L. L. Chave. *Afinidad* **25**, 498–503 (1948) (through *Chem. Abstr.* **43**, 2777*a* (Apr. 10, 1949)).

The Freundlich adsorption isotherm can be applied to experimental data for the adsorption of Durazol Blue 3R-200 (an azo dye) on viscose rayon. A comparison of the effects of NaCl and Na_2CO_3 in the dyebath showed Na_2CO_3 to have the stronger flocculating action. *Text. Research J. Dec. 1949*

Damping-Capacity Measurements of Fibers

Measurement of modulus and damping capacity in torsion and in bending for wool and other textile fibres. J. P. A. Lochner. *J. Text. Inst.* **40**, T220–31 (Apr. 1949).

Methods are described for the determination of the damping capacity for torsion and for bending of fibers. A method for the determination of Young's modulus for bending of short fibers is also described. For fibers having a homogeneous structure, the measurements of damping capacity in torsion and in bending are in good agreement; for fibers having a heterogeneous structure, the damping capacity for bending is not necessarily the same as that for torsion. L. P. Witnauer *Text. Research J. Dec. 1949*

Density and Bulk of Staple Rayon

Staple rayon. III. Density and fiber bulk. H. Böhringer and W. Graf. *Melliand Textilber.* **27**, 106–10 (1946); *Chem. Zentr.* **1947**, I, 575; cf. *C.A.* **28**, 2500[1] (through

* A list of periodicals, the abbreviations used in reference to articles, and the addresses of publishers of English-language publications is given in the January, 1949, issue, page 46.

Chem. Abstr. **43**, 2778*c* (Apr. 10, 1949)).

The ordinary method of determining specific gravity yields inaccurate and scattered values. Not only the fiber itself, but a mixture of fibers, empty spaces, and admixed materials is measured. The value obtained with water as a measuring fluid is consistently higher than that obtained with organic liquids. The maximum value is obtained by the buoyancy method after steeping in hot water under high vacuum in a special apparatus. Liquids of high molecular weight and low density, such as triolein, are best suited for measurement of the bulking value. Procedures and calculations for the measurement of density and fiber bulk are given.

Text. Research J. Dec. 1949

Dyeing Wool

The combination of wool with acids—a quantitative interpretation in terms of the Donnan theory of membrane equilibrium. L. Peters and J. B. Speakman. *J. Soc. Dyers and Colourists* **65**, 63–71 (Feb. 1949).

The purpose of this paper is to show that the internal hydrogen ion concentration, which cannot be measured directly, can be calculated, and that the Donnan theory is capable of giving a more precise interpretation of the titration curves than the expressions derived from other considerations by Steinhardt and Harris, or by Gilbert and Rideal. The work of these authors is reviewed. A quantitative interpretation of the combination of wool with hydrochloric acid, sulfuric acid, and hydrochloric acid in the presence of different concentrations of potassium chloride has been obtained in terms of the Donnan theory of membrane equilibrium. The course of combination is determined by the pH inside the fiber, which can be calculated although it cannot be measured directly. When the amount of combined acid is plotted as a function of the "internal" pH, the mid-point of the titration curve is found to lie between pH 4.15 and 4.35 in the case of hydrochloric acid, as would be expected if combination were due to back-titration of the carboxylic groups of salt linkages. Similarly, in the case of sulfuric acid, the mid-point is at pH 4.45, and the unification of the hydrochloric acid and sulfuric acid titration curves, as well as the agreement between the observed and expected pH values, affords strong evidence in support of the Donnan theory. In addition, it has been shown that the curves obtained by titrating wool with hydrochloric acid in the presence and absence of potassium chloride, the amounts of potassium chloride being sufficient to give a constant chloride ion concentration, are unified when the amounts of combined acid are plotted against the calculated "internal" pH values. The Donnan theory also provides a precise interpretation of the manner in which the pH corresponding to half-maximum combination with acid varies with changing salt concentration. C. Amick

Text. Research J. Dec. 1949

Differential Dyeing Test

Application to viscose rayon of the differential dyeing test for cotton maturity. W. Armfield and J. Boulton. TEXTILE RESEARCH JOURNAL **19**, 212–14 (Apr. 1949).

This is a report on the application to viscose rayon in the form of staple fiber of a technique described by Goldthwait *et al.*, which involves a dyeing technique in which normal thick-walled hairs assume a red, and thin-walled a green color.

Text. Research J. Dec. 1949

Elastic Modulus of Textiles

Measurement of hysteresis and dynamic elastic modulus of textile yarns and cords. G. Palandri. *Rubber Age* (N.Y.) **64**, 45–52 (1948) (through *Chem. Abstr.* **43**, 2439*d* (Mar. 25, 1949)).

The few currently employed methods for measuring the dynamic modulus and hysteresis loss of textile fibers are reviewed and discussed. A new apparatus and technique of the type used for rubber (cf. *C.A.* **42**, 9233*b*) are described and illustrated, whereby cords and yarns stretched by a permanent static load are deformed in tension at frequencies of 20 to 200 cycles per sec., with dynamic tension strains of 0.02 to 0.08%, and in a temperature range of 20°–65°C. Experimental results obtained on cords and on single yarns of the corresponding materials are presented and discussed. With continuous and with long fibers, the hysteresis loss as a function of dynamic tension strain followed a quadratic law, and the dynamic modulus E was independent of tension strain. On the other hand, with short-fiber textiles, E decreased with increase in the dynamic tension strain. Furthermore, E was independent of the frequency in the range above 100 cycles per sec., and the hysteresis losses increased in proportion to the frequency. Comparative data on the hysteresis losses and moduli of some of the most widely used textile fibers are presented with a view to showing the practical application of such data.

Text. Research J. Dec. 1949

Fractionation of Starch

The fractionation of starch. I. The estimation of amylose in the presence of amylopectin. R. S. Higginbotham and G. A. Morrison. *J. Text. Inst.* **40**, T201-7 (Apr. 1949).

Potentiometric estimation of amylose in the presence of amylopectin is more accurate, though somewhat less convenient, than the colorimetric procedure. The former also has the advantage that the conditions can be so chosen that the pure unfractionated amyloses of the common starches absorb the same amount of iodine while the corresponding amylopectins absorb a negligible amount. In colorimetric procedures allowance must be made for the fact that iodine complexes of the amyloses and amylopectins of different starches have different absorption characteristics. A simple potentiometric procedure is described in which the only special equipment required is a sensitive galvanometer. In the potentiometric technique, the second stage of the absorption of iodine by pure amylose is not linear but exponential, so that the customary

procedure of extrapolating the two "linear" portions of the bound iodine *vs.* free iodine curve and characterizing the amylose by their point of intersection is not valid. However, pure or nearly pure amyloses are adequately characterized by their iodine absorption in a solution which is 0.05*N* with respect to both KCl and KI with a free iodine concentration of $10^{-3}N$. Under these conditions pure amylose absorbs 21.0% iodine, while amylopectin absorbs 0.1–0.5%. In analyzing mixtures in which the amylopectin predominates, the amylose content is most accurately determined by dividing the percent of iodine bound at the point of discontinuity on the absorption curve by the percent of iodine bound by the pure amylose at the same concentration of free iodine. When the mixture contains more amylose than amylopectin, the proportion of amylose is given with sufficient accuracy by the ratio of the percent of iodine bound at a free iodine concentration of $10^{-3}N$ to the iodine absorption of the pure amylose. The colorimetric procedure examined was the modification by Bourne and Peat (*J. Chem. Soc.* **1945**, 877) of the method of Hassid and McCready (*J. Am. Chem. Soc.* **65**, 143 (1943)), except that different means were employed in dissolving the materials. R. O. Steele

Text. Research J. Dec. 1949

The fractionation of starch. II. The separation of amylose and amylopectin. R. S. Higginbotham and G. A. Morrison. *J. Text. Inst.* **40**, T208–19 (Apr. 1949).

Up to the present, the complete separation of the components of starch through the use of organic solvents to precipitate the amylose has not been achieved, and it is still not certain that starches contain only two sharply differentiated substances. The present investigation is to determine whether sago, maize, potato, and tapioca starches can be separated quantitatively into two fractions consisting solely of amylose and amylopectin. "Iodine absorption" was used as a criterion of purity, but the possibility still remains that the fractions are heterogeneous in chemical nature as well as in molecular size. The amylopectin was purified by repeated recrystallization from dilute butanol-saturated aqueous solutions. The iodine absorption of the pure amylose was 21.0%. Amylopectin cannot be purified, so that its purity is determined by the conditions under which the original precipitation takes place. The apparent removal of traces of amylose from amylopectin by cellulose, as indicated by an iodine-staining technique, was shown to be due to complexing of the amylose with methanol-soluble fatty impurities in the cellulose. Fairly complete separation of sago, tapioca, and potato starches into two well-defined fractions was achieved using various methods of dispersion, with pyridine or butanol as precipitating agents for the amylose. The results with maize starch suggest that even the completely dispersed material contains aggregates which include 20% of the total amylose and 80% of the amylopectin. The nature of the bonds which cause these aggregates is obscure, but they are probably normal primary valence bonds because hydrogen bonds or van der Waals forces would presumably be broken by such dispersing forces as aqueous pyridine at 120°C or normal KOH. Since absolute quantitative separation of the other starches was not achieved, the possibility still exists that such aggregates occur in them also. However, the amylose bound in such aggregates cannot exceed 3% for sago and potato starches, or 6% for tapioca. R. O. Steele

Text. Research J. Dec. 1949

Friction Measurement

Measurement of friction between single fibers. IV. Influence of various oxidizing and reducing agents on the frictional properties of wool fibers. J. Lindberg and N. Gralén. TEXTILE RESEARCH JOURNAL **19**, 183–201 (Apr. 1949).

Previous articles in this series appeared in the Sept., 1947, May, 1948, and Aug., 1948, issues of TEXTILE RESEARCH JOURNAL. In this study a twist friction meter, previously described, was employed for measuring the effects on the frictional properties of wool fibers of various chemical treatments. It is concluded that the frictional behavior of wool and its change due to treatments with different reagents is explained by the histological structure of the outer layers of the wool fiber.

Text. Research J. Dec. 1949

Gelation of Ethyl Cellulose

The gelation of aqueous solutions of ethylcellulose on heating. S. Sönnerskog. *Acta Chem. Scand.* **2**, 523–6 (1948) (in English) (through *Chem. Abstr.* **43**, 3611*d* (May 10, 1949)).

The fact that solutions of ethylcelluloses showing a degree of substitution between 1.2 and 1.4 increase suddenly in η on cooling is explained by an analysis of the possibilities of cross-linking and simple orientation of H_2O dipoles with regard to the cellulose OH. Gelation on heating is shown to be due to a removal of purely oriented H_2O molecules.

Text. Research J. Dec. 1949

Detection of Oxy- and Hydrocellulose

New methods for the detection of oxy- and hydrocellulose. F. Müller. *Melliand Textilber.* **27**, 93–5 (1946); *Chem. Zentr.* **1947, I**, 574; cf. *C.A.* **33**, 4018[8] (through *Chem. Abstr.* **43**, 2777*b* (Apr. 10, 1949)).

Keto and aldehyde groups can be determined with phenylhydrazine by modification and coupling with diazonium compounds. 8-Hydrazino-1-naphthol-3,6-disulfonic acid or any other monoarylhydrazine can be used. For coupling, diazotized sulfanilic or naphthionic acid is suitable, as well as Fast Blue Salt B or the tetrazotized diaminostilbenedisulfonic acid. The procedure is: 2 samples are boiled ½ min. and 1 hr., respectively, in a 1% solution of p-$NH_2NHC_6H_3SO_3H$. The samples are rinsed and treated ½ hr. in a weakly alkaline solution of Variamine Blue Salt FG or Fast Blue Salt B. After rinsing and washing, a brownish-red color on the first

sample indicates oxycellulose and a violet color on the second sample, hydrocellulose. Hydrocellulose cannot be detected in the presence of oxycellulose. 4-Hydrazino-2,5-dichlorobenzenesulfonic acid responds only to oxycellulose. The preparation of 8-hydrazino-1-naphthol-3,6-disulfonic acid is given.

Text. Research J. Dec. 1949

Mechanical Property Measurements by Electromagnetic Transducers

Measurements of the mechanical properties of polymer solutions by electromagnetic transducers. T. L. Smith, J. D. Ferry, and F. W. Schrimp. *J. Applied Phys.* **20**, 144–53 (Feb. 1949).

A concentrated polymer solution is sheared by a rod oscillating axially with a very small amplitude in a closed tube. The rod is driven by a coil in a magnetic field. From electrical measurements on the coil the mechanical resistance and reactance of the system are calculated by transducer relationships. Equations are given for obtaining the dynamic viscosity, η', and rigidity, G', of the solution. In the case of some polymer solutions, the audiofrequency range covered by the present apparatus falls in the dispersion zone where η' and G' change rapidly with frequency. In other cases the frequency range covered appears to be at the upper end of the dispersion zone; η' is far less than the viscosity in steady flow, and G' changes very little with frequency. The advantages and the limitations of the method are discussed. Authors

Text. Research J. Dec. 1949

Uronic Acid Determination

Manometric method for the estimation of milligram quantities of uronic acids. M. V. Tracey. *Biochem. J.* **43**, 185–9 (1948); cf. *C.A.* **43**, 1130*i* (through *Chem. Abstr.* **43**, 2663*d* (Apr. 10, 1949)).

The method depends on the decomposition of a not more than 50-mg. sample with 0.25 ml. 12% HCl (wt./wt.) in a sealed tube at 111°C. and the manometric determination of the CO_2. The details for preparation of the tubes, etc., are given. A large number of substances were tested and some were found to cause serious interference with the CO_2 yield from uronic acids. The method is only useful for routine analysis of small amounts of material.

Text. Research J. Dec. 1949

Determining Starch Viscosity

Determining starch viscosity. W. G. Bechtel. *Textile Inds.* **113**, 92–4 (June 1949).

A description and schematic drawing of a newly developed viscometer suitable for testing starch compounds used in textile sizing, finishing, and printing processes. Viscosity is recorded continuously by means of a dynamometer which measures the power required to drive an impeller through the compound tested. A. L. Landau

Text. Research J. Dec. 1949

Estimating Intrinsic Viscosity

Methods of estimating intrinsic viscosity. F. W. Billmeyer. *J. Polymer Sci.* **4**, 83–6 (Feb. 1949).

9 equations relating dilute-solution viscosity of high polymers to intrinsic viscosity are given. Some of these are applicable to a given polymer-solvent system and can be useful once the constants are determined. The applicability of some of these equations to polymethyl methacrylate in methylene dichloride is illustrated.

Text. Research J. Dec. 1949 E. D. Klug

Grade Determination of Wool

Easier grade determination by measurement in wool top. F. M. Wadley, Elroy M. Pohle, and Werner A. Mueller. TEXTILE RESEARCH JOURNAL **19**, 278–82 (May 1949).

Measurements of wool-top fiber diameter are used to determine whether the lot average falls within certain predetermined limits. If the lot average is near the middle of a grade range, fewer measurements will be needed for assurance than if the average is near the border. A table of limits of sample means for each grade is arranged, within which 100 fibers is enough; wider limits for 200, 300, and greater numbers of fibers are shown. Experimental sampling which tested these concepts is described. Weaknesses of frequency distribution estimates are discussed, and greater use of the standard deviation is suggested. Authors

Text. Research J. Dec. 1949

Orientation in Viscose Fibers

Viscose rayon fibres. II. The orientations of skin and core. J. M. Preston and K. I. Narasimhan. *J. Text. Inst.* **40**, T327–37 (May 1949).

Using a fiber refractometer and the Becke method, the refractive indices of the skin and the core of viscose rayon fibers were determined. Data are reported for several series of fibers with a range of orientations. Skin and core structures are proposed and discussed in detail. A theoretical, quantitative relationship between the structures is considered. L. P. Witnauer

Text. Research J. Dec. 1949

Crystallite Orientation of Cellulose Fibers

A new method of evaluation of the crystallite orientation of cellulose fibers from x-ray data. P. C. Tsien. TEXTILE RESEARCH JOURNAL **19**, 330–41 (June 1949). **Appendix.** *Ibid.* **19**, 416–20 (July 1949).

Based upon the assumption that the number of crystallites included in any definite angular interval is a function of the angle to the fiber axis, a method is devised by which the equatorial intensity of the 002 diffraction spot can be analyzed into its components to give the angular distribution curve of crystallites around the fiber axis. Values of average sine are calculated and these can be checked by average square sine values calculated from the other two nearly perpendicular paratropic planes. Moderate agreement is obtained. Author

Text. Research J. Dec. 1949

Tenacity-Testing Apparatus

A new tenacity-testing apparatus for fabrics, paper, etc. H. Sulser. *Textil-Rundschau* 4, 49–53 (1949) (through *Chem. Abstr.* **43**, 3202*a* (Apr. 25, 1949)).

The apparatus operates by puncturing the test sample with a hard, polished sphere. The tenacities and elongations at break observed with 19 different fabrics were similar to those obtained by the conventional strip-tension method of testing.

Text. Research J. Dec. 1949

Single Yarn *vs.* Skein Breaking-Strength Test

Single yarn and skein breaking strength tests as evaluation of drafting procedures. E. Toenissen. *Textil-Praxis* **4**, 101–3 (Mar. 1949).

The author recommends skein breaking-strength tests when accurate evaluation of yarn quality is desired. 20 skeins or 70 single strands each from 10 packages were considered an appropriate sampling when high-quality rayon staple was used to evaluate the effects of several drafting systems on yarn quality. J. F. Krasny

Text. Research J. Dec. 1949

Fiber Tensile Values

A comparison of fiber tensile values obtained on the Pressley Tester and Scott IP-4 at different test speeds. J. K. Phillips. TEXTILE RESEARCH JOURNAL **19**, 274–7 (May 1949).

A comparison was made of fiber tensile values obtained on the Scott IP-4 machine and the Pressley Tester at their normal test speeds and also at comparable test speeds. The effect of elapsed time to break on the strength of fibrous materials was shown to be very great at the test speeds normally used on the Pressley Tester as compared to those on the Scott IP-4 machine.

Text. Research J. Dec. 1949 Author

Testing of Rayon Staple

Simplification of testing procedures for rayon staple. H. Köb. *Textil-Praxis* **4**, 155–9 (Apr. 1949).

A.S.T.M., B.I.S.F.A. (Bureau International pour la Standardization des Fibres Artificielles), and DIN (German) testing procedures are compared and criticized. Definitions, sampling, regain, staple length and fineness, and tensile-strength tests are discussed. J. F. Krasny

Text. Research J. Dec. 1949

Titration of Viscose

Potentiometric titration of viscose. P. Herrent and G. Jnoff. *J. Polymer Sci.* **3**, 834–49 (Dec. 1948).

It has been found, by interpretation of the curve for the potentiometric titration of viscose with 0.1*N* $AgNO_3$, that the sulfur compounds of viscose exist in the ortho form. This leads to a new theory of the ripening of viscose. Authors

Text. Research J. Dec. 1949

Wetting of Textiles

Investigations on the action of wetting agents. I. Wetting of textiles. II. Practical results of the investigations. J. Jensen. *Textilteknik* **7**, 21–9 (1949) (based on Communication No. 33 of the Danish Textile Research Inst.) (through *Chem. Abstr.* **43**, 3623*h* (May 10, 1949)).

The report refers to textile wetting agents, in which the Danish textile industry is interested (not specified), and comprises: measurements of the wetting power by the surface tension as a valuable supplement to practical measurements (hydrometer, Herbig (cf. *C. A.* **20**, 1142), and Drave methods), all of which are described in detail.

Text. Research J. Dec. 1949

Non-Felting Wool

The treatment of wool with acid permanganate solutions. P. Alexander, D. Carter, and R. F. Hudson. *J. Soc. Dyers and Colourists* **65**, 152–61 (Apr. 1949).

Wool can be rendered non-felting by treatment with dilute solutions of permanganate at a pH less than 2; the optimum conditions for treatment are described. Wool treated in this way does not felt when left even for very long periods in a washing machine, but does felt as much as untreated wool when exposed to a milling action. Wool which has received prolonged permanganate oxidation treatment acquires some resistance to felting in a mill. Permanganate-treated wool shows no resistance to felting when washed in acid in a washing machine or a mill. The implications of these results for the theory of felting are discussed. The damage done to the wool by permanganate treatment is slight and has been assessed in a number of ways. The nature of the reaction has been studied from analytical and kinetic viewpoints, and it is shown that the chief reaction is an oxidation of the disulfide bond, the rate being controlled by diffusion. There is a fundamental difference between the actions of acid and alkaline permanganate. A secondary reaction between the permanganate and the tyrosine in the wool is responsible for the yellowing. Three equivalents of oxygen are consumed per molecule of tyrosine. C. Amick

Text. Research J. Dec. 1949

Laboratory Spinning Techniques

Repeatability and tolerances of laboratory spinning techniques. Ruby E. Stewart and L. E. Parsons. TEXTILE RESEARCH JOURNAL **19**, 283–7 (May 1949).

In setting up and operating a spinning laboratory, a number of bench marks must first be established. Among the most important of these are: (1) size of test necessary for reliable results; and (2) repeatability or experimental error. If the first item is not established, results may be accepted on insufficient data; or, vice versa, time may be wasted in running tests longer than necessary. If the second yardstick is not determined, it is impossible to interpret the data accurately, since it would not be known when to attach significance to test results. In order to settle these questions, therefore, 2 series of tests were conducted, in each of which the cotton mix was held constant, and the manufacturing was performed with as nearly identical conditions as

possible. These tests represent approximately 54,000 spindle hours, and should, therefore, give conclusive evidence of the repeatability of the spinning test under controlled conditions. Data given indicate that good repeatability of results may be obtained on the same cotton and that properly conducted spinning tests may be made on different cottons and the results compared directly. However, in interpreting data from other tests it must be remembered that in order for the differences between cottons to be significant they must be greater than the differences shown in these tests, since the differences obtained in this study constitute the experimental error. Authors

Text. Research J. Dec. 1949

Treatment of Data

Use of probability paper for estimating the mean and standard deviation of normally distributed textile test data. John D. Tallant. TEXTILE RESEARCH JOURNAL **19**, 270–3 (May 1949).

Commercially available "probability paper" is discussed, and its use as a tool for rapidly obtaining the mean and standard deviation of data is demonstrated. A table comparing graphical and calculated results is given. Mathematical theory and a discussion of sources of error and their magnitude conclude the article. Author

Text. Research J. Dec. 1949

CHEMICAL AND PHYSICAL RESEARCH

★

Hydrolysis of Cellulose

Hydrolysis of wood cellulose. F. A. Abadie. *Compt. rend.* **226**, 1539–41 (1948); cf. *C. A.* **40**, 1311[6] (through *Chem. Abstr.* **42**, 8464*i* (Nov. 10, 1948)).

The effect of H_2SO_4 concentration on complete hydrolysis to hydrocellulose (*I*) was determined. It was found that the time of heating (*t*) was inversely proportional to the concentration of acid (*C*), the amount of acid having no effect on *t*. With *C* constant, *t* and the quantity of (*I*) remain constant. For industrial applications, *C* is 7.5–30%. Below 7.5%, heating has to be continued too long. Above 30%, in addition to the formation of glucose, organic acids, MeOH, and furfural are formed also. The curve *t* vs. *C* is a hyperbola. Within the industrial limits of *C*, the empirical formula $t = -C + 44$ approximates actual conditions.

Text. Research J. Dec. 1949

Photochemistry of Cellulose

The photochemistry of cellulose: Effect of water vapor and oxygen in the far and near ultraviolet regions. H. F. Launer and W. K. Wilson. *J. Am. Chem. Soc.* **71**, 958–62 (Mar. 1949).

In the far ultraviolet region (254 millimicrons) water vapor retards and oxygen is without effect on the decomposition of cellulose, as measured by cuprammonium D.P. and α-cellulose content. In the near ultraviolet region (360–388 millimicrons) both of these effects are reversed. These phenomena are explained on the basis of the relative values of bond energies in the molecular chains and the energies of the photons involved. Ultraviolet photons have sufficient energy to disrupt the —C—C— or —C—O— bonds, whereas most near ultraviolet photons do not and require the participation of oxygen. The retarding action of water vapor in the far ultraviolet region is ascribed to interchain water bridging with the hydroxyls on carbons 2 or 3. This supports the theory that a part of the moisture in cellulose is in a fundamental chemical combination. A. R. Macormac

Text. Research J. Dec. 1949

Degree of Structural Order of Cellulose and Cellulose Acetate Yarns

The effect of variations in degree of structural order on some physical properties of cellulose and cellulose acetate yarns. Robert W. Work. TEXTILE RESEARCH JOURNAL **19**, 381–93 (July 1949).

It is shown by means of x-ray diffraction diagrams that cotton, a highly crystalline and oriented material, gives a triacetate of low crystallinity which may be rendered more crystalline by annealing. This triacetate is partially hydrolyzed to form the secondary cellulose acetate used in textile yarns, which gives an x-ray pattern showing a highly amorphous structure. Although steric effects prevent increases in crystallinity by annealing, this type of yarn can be oriented, the degree of orientation depending upon the conditions under which stretching of the yarn takes place. By swelling and allowing limited mobility, this orientation may be increased over that produced by dry stretching. Cellulose acetate fibers may be converted into highly crystalline celluloses, the orientation of the original material carrying over into a hydrolyzed product. The load-elongation characteristics of families of these 2 types of yarns are described and the effects of orientation are discussed. The decrease in lateral strength, due to orientation, is illustrated by means of electron micrographs of the material. The relationship between orientation in series of cellulose acetate and corresponding cellulose yarns having greater or lesser degrees of orientation and the sonic moduli of these materials are illustrated. Possible explanations are suggested. Dye retention similarities between mature cotton and slightly oriented cellulose yarn on the one hand and immature cotton and unoriented cellulose yarn on the other hand are given to indicate that orientation may be one basic difference between mature and immature cottons.

Text. Research J. Dec. 1949 Author

X-Ray Studies of Cellulose

Small-angle scattering of x-rays and the micellar structure in cellulose fibers. A. J. N. Heyn. *J. Am. Chem. Soc.* **71**, 1873–5 (May 1949).

There is a close relationship between the intermicellar distances in cellulose fibers and the intensity distribution in small-angle x-ray scattering. Additional evidence to support this conclusion is based on studies of swelling in water, potassium hydrox-

ide, and cuprammonium hydroxide. Depositing of gold crystals, crystals of sodium chloride, or saccharose changed the x-ray pattern, as was expected. (See also *J. Am. Chem. Soc.* **70**, 3138 (1948) and TEXTILE RESEARCH JOURNAL **19**, 163–72 (1949).) A. R. Macormac

Text. Research J. Dec. 1949

Contact Angle on Fibers

Contact angles. A. B. D. Cassie. *Discussions Faraday Soc.* **1948**, No. 3, 11–16 (through *Chem. Abstr.* **43**, 1239*e* (Feb. 25, 1949)). The relation of contact angles to surface structure is outlined. The difficulty of reproducing a "smooth" surface doubtless is the cause for so many published values of contact angles. Despite this, the absolute values of these angles give a useful relation between measurable roughness and angle. This treatment may be extended to heterogeneous surfaces. Advancing contact angles only appear to give agreement between theory and experiment and probably no phenomenon in *textiles* that involves receding contact angles has been explained satisfactorily. The reason for this is their instability. The difference between the advancing and receding contact angles is discussed in terms of the modern theory of multimolecular adsorption. This theory indicates that the advancing angle will be unique whereas the receding one will generally be less than the advancing angle and need not have a unique value.

Text. Research J. Dec. 1949

Refractive Index of Cotton During Growth

Growing process of cellulose fiber. I. Change in refractive index during the growing period of cotton cellulose. K. Sofue, R. Yano, and Y. Koshimizu. *J. Soc. Chem. Ind. Japan* **47**, 558–60 (1944) (through *Chem. Abstr.* **43**, 1462*a* (Feb. 25, 1949)).

Arrangement of cellulose at the first stage of the growth of Upland cotton fiber was determined by measuring η_γ and η_α in the direction of the fiber and that perpendicular to it, respectively. Starting from the date of drop of flower, η_γ decreased to its minimum value in 10–12 days, then increased again rapidly till it attained 1.571 on the 18th day, which was about equal to the value of the matured fiber. The value of η_α decreased suddenly on the 10–12th day and continued to decrease gradually, having the value 1.532 on the 18th day, which was still slightly higher than the value of matured fiber. The value of $\eta_\gamma - \eta_\alpha$ was 0.015, 0.029, 0.034, 0.039 on 10th, 12th, 14th, and 18th days, respectively, the final value being 0.050.

Text. Research J. Dec. 1949

Tendering of Cotton

The degradation of cotton during atmospheric exposure, particularly in industrial regions. E. Race. *J. Soc. Dyers and Colourists* **65**, 56–63 (Feb. 1949).

Consideration of the exposure of cellulosic material to the action of weathering agencies involves the examination of the effects of 3 natural agents—air, sunlight, and atmospheric moisture. Estimation of the degradation of cellulose is not simple. The breakdown of glycosidic linkages implies hydrolysis rather than oxidation as the primary step. Simple hydrolysis would result in the formation of reducing groups, but if the cleavage is followed by oxidation, the product may not exhibit a greater reducing power. Therefore, the increased reducing power of oxycellulose is not necessarily a full measure of the extent to which cleavage has occurred. Cellulose is not attacked by molecular oxygen, but 3 possible explanations are listed to account for the oxidation of cellulose during exposure to atmospheric oxygen. They are: (1) the cotton substrate acts as an activator and the oxygen is converted into ozone, which degrades the cellulose; (2) photochemical degradation is a precursor of oxidation; and (3) ultraviolet radiation activates, without degrading, the cellulose, which is thereafter capable of being attacked by gaseous oxygen. Gray yarn purified by extraction with alcohol and ether, then successively treated with 1% sodium hydroxide, 1% sodium hypochlorite, and 1% acetic acid, was exposed for 20 wks. during the summer. This resulted in a loss in breaking strength of about 50%, an increase in fluidity in cuprammonium hydroxide, a large drop in the degree of polymerization, a large increase in the copper number, and an increase in the carboxyl content. These data indicate that under the action of light and air, the cellulose is converted into an oxycellulose, mainly of the reducing type, in which there is a preponderance of carbonyl groups, a shortening of the average chain length, and a very small increase in the proportion of carboxyl groups. However, in the winter, the tensile strength loss was greater than in the summer, apparently due to the greatly increased acidity of atmospheric gases in winter compared with that in summer, particularly in industrial regions. Confirmation that oxidation, as distinct from hydrolysis, is greater in summer than in winter is supplied by the fact that production of carboxyl groups, which is small in summer, is even smaller in winter. C. Amick

Text. Research J. Dec. 1949

Mechanical Work of Detergency

Detergent action—mechanical work as a measure of efficiency of surface active agents in removing soil. O. C. Bacon and J. E. Smith. *Ind. Eng. Chem.* **40**, 2361–70 (Dec. 1948).

The purpose of this paper is to establish the existence of a quantitative relationship between the concentration of a surface-active detergent in water and the mechanical work required in removing soil in a detergent process. In addition to accomplishing this purpose, a method of calculating the percent of colored soil removal from reflectance data is presented. An equation of the curves relating the percent soil removal and the factors of detergent concentration, applied force, and time at a given temperature is developed also. The principles established provide a basis for developing

a comprehensive method for the evaluation of detergents in the removal of soil. Authors

Text. Research J. Dec. 1949

Perspiration and Bacteria Damage

The influence of perspiration on the bacterial damage of fibers and its prevention. M. Nopitsch. *Melliand Textilber.* **28**, 161–4 (1947) (through *Chem. Abstr.* **42**, 8482*d* (Nov. 10, 1948)).

The effect of human perspiration on the bacterial damage of wool, cotton, and viscose fibers was studied. Physiological salt solution adjusted to pH 4.5, 7.0, and 8.5 was used as media to simulate perspiration. The organism used was *Bacillus mesentericus*. Separate samples were given various treatments, including washing, bleaching, loading with $Cr(OH)_3$, and impregnation. It was found that pH exerted the most important influence, especially for wool. The alkaline samples showed the greatest damage, while those in acid media were almost unaffected. The damage was less pronounced on cotton and least extensive on viscose. $Cr(OH)_3$ had a protective action for wool which was almost independent of the perspiration effect.

Text. Research J. Dec. 1949

Photochemical Degradation

Some aspects of the photochemical degradation of nylon, silk, and viscose rayon. G. S. Egerton. TEXTILE RESEARCH JOURNAL **18**, 659–69 (Nov. 1948).

The vat dyes that are particularly effective in increasing the photochemical degradation of nylon, silk and viscose rayon are capable of increasing the degradation of undyed cotton that is simultaneously irradiated in their vicinity. The experiments took the form of irradiating a sheet of yarn composed of alternate dyed and undyed threads not in contact with one another. The dyed threads used included nylon, silk, and vicose rayon yarns dyed with various vat dyes. Many of the dyed yarns have a considerable effect upon the degradation of adjacent undyed yarns of cotton or silk, but the same dyed yarns generally have only a small or negligible effect upon the degradation of undyed yarns of nylon or viscose rayon. These results are apparently due to the greater resistance of the latter textile materials to oxidation by the volatile agent (hydrogen peroxide), which is responsible for the "action at a distance." In some cases—for example, dyed nylon—there is evidence that although the volatile agent is produced by the dye in a relatively large amount it is not responsible for the major proportion of the degradation of the dyed yarn. The effect of humidity on the rate of photochemical degradation of textile materials dyed with active vat dyes appears to be closely related to the ease with which the textile fiber is oxidized by the volatile agent. These results are interpreted in terms of a theory in which the photochemical degradation of the textile material is represented as the result of oxidation by activated oxygen and/or hydrogen peroxide. The relative effectiveness of these two oxidation processes depends upon the particular experimental conditions and the nature of the textile fiber. Author

Text. Research J. Dec. 1949

Fiber Deterioration

The fungi concerned in fiber deterioration. I. Their occurrence. P. B. Marsh and K. Bollenbacher. TEXTILE RESEARCH JOURNAL **19**, 313–24 (June 1949).

A review of the literature and certain new findings are presented which relate to the types of fungi which occur on cellulosic textile fibers under various practical exposure conditions. Numerous observations, some original and others assembled from the literature, indicate that the following fungi are commonly found growing on fibers in particular types of situations: *Alternaria*, *Cladosporium herbarum*, and *Fusarium* (especially *F. moniliforme*) on cotton which has undergone weathering in the field before harvest; *Alternaria* and *Cladosporium herbarum* on cotton fabric in relatively short-term moderate- or high-light weather exposures, with *Phoma* and related forms, *Leptosphaeria* and related forms, and *Pullularia pullulans* appearing after longer periods under the same conditions; *Alternaria*, *Cladosporium herbarum*, *Pullularia pullulans*, and, under some conditions, *Fusarium* on dew-retting flax and hemp; species of *Aspergillus*, *Penicillium*, *Stachybotrys*, *Chaetomium*, and probably other fungi on cotton and other natural fibers in unprocessed or in textile form in humid storage; *Aspergillus fumigatus* on jute which has undergone microbiological damage in the bale; *Halophiobolus* and certain other unusual salt-water-adapted forms on decaying cordage in marine exposures. Fungi other than the above-named may occur commonly under the conditions mentioned, but if they do this appears not to have been reported frequently or in any detail in the literature. Soil-contact exposures are believed to involve a very wide range of fungus forms, including numerous genera and species which have not been observed to occur commonly in moderate- or high-light above-ground exposures. Information is presented which indicates that resistance on the part of the fungus to sunlight is an important factor in determining which fungi grow on fibers in different types of exposures. Differences among the fungi in moisture requirements and in temperatures favorable for growth are also important.

Text. Research J. Dec. 1949 Authors

Diffusion of Dyes

The diffusion of organic dyes through semipermeable membranes. N. Riehl and K. Waschiczek. *Z. anorg. Chem.* **253**, 45–53 (1945); *cf.* following abstr. (through *Chem. Abstr.* **43**, 2486*f* (Apr. 10, 1949)).

The unexpectedly high permeability of semipermeable films for dyes probably depends on the fact that the solutions dealt with are very dilute (of the order of 0.1 to 0.001 g. per 100 g. of H_2O). Because of the higher adsorption (on a percentage basis) from dilute solutions, the osmotic coefficient (in the relation

$C = C_0 e^{-t}$) depends on the concentration. The coefficient decreases with increasing concentration.
Text. Research J. Dec. 1949

The diffusion of dissolved substances through semipermeable walls. N. Riehl and N. Trubetzkoy. *Z. anorg. Chem.* **253**, 54–70 (1945); *cf.* preceding abstr. (through *Chem. Abstr.* **43**, 2486g (Apr. 10, 1949)).

Films were prepared by impregnating very thin cellophane foil with precipitated Cu ferrocyanide (*I*). The semipermeable foils permit not only a separation of colloids and crystalloids, but also a separation of subcolloids and of crystalloids from one another. Dissolved substances of small molecular weight can be easily dialyzed from substances with a molecular weight of 1,000 or greater. The pairs HCl-glucose and H_2SO_4-glucose were studied; results with impregnated cellophane and with ordinary cellophane were compared. In comparison with glucose (*II*), the acid diffuses more rapidly the smaller the concentration, and impregnating the film with *I* improves the separation between acid and *II* about 1.5 times. Under the optimum conditions the acid diffuses 20 times as fast as *II*. The separation of *II* from 3 amino acids was also studied. The ratio of rates of diffusion of the acids and *II* varied from 1.0 to 18, depending upon the amino acid and the conditions.
Text. Research J. Dec. 1949

A diffusion problem in which the amount of diffusing substance is finite. A. H. Wilson. *Phil. Mag.* **39**, 48–58 (1948) (through *Chem. Abstr.* **43**, 2839g (Apr. 25, 1949)).

Effects arising in a dye bath are considered theoretically. Finiteness of the dye bath is considered particularly. The simplest law of adsorption of the dye that gives a nontrivial result is chosen. A complete solution is obtained without recourse to numerical methods. The analysis can be applied, either directly or with trivial modifications, to many problems. Three problems are solved and 2 different methods, depending, respectively, on an expansion in orthogonal functions and on the Laplace transform, are used. These problems are: diffusion into a lamina, diffusion into a cylinder, diffusion when the rate of adsorption is infinitely rapid, and diffusion when rates of adsorption and diffusion are comparable.
Text. Research J. Dec. 1949

Double Refraction

Relation between the double refraction and the strength and elongation of artificial fiber. I. Case of isotropic regenerated fiber made anisotropic by strechning. S. Okajima and H. Watanabe. *J. Soc. Chem. Ind. Japan* **48**, 87–8 (1945) (through *Chem. Abstr.* **42**, 7039*a* (Sept. 20, 1948)).

For the purpose of studying the effect of micelle orientation and the stretching conditions which produce micelle orientation on the strength of fiber, the relation between the double refraction, Γ, and the tensile strength and elongation of fiber was examined. The wet tensile strength increased linearly with Γ, and the curves for samples of different degrees of polymerization, *P*, had nearly the same slope. The strength at Γ = 0 was proportional to 1 *P*. The change in the tensile strength in the dry condition was irregular. Wet elongation increased with the increase in *P*, but it was nearly constant when *P* was less than 500. The ratio, *R*, of wet strength to dry strength decreases with increase in Γ, but *R* increases when Γ is further increased. It is noteworthy that at Γ = 0 for large *P*, *R* is 1.

II. Case of fiber regenerated by removing copper under tension. —Cuprammonium cellulose fiber prepared by regenerating under tension was compared with fibers prepared by stretching dry after regeneration. Regeneration under tension is very effective in the promotion of micelle orientation. The relations among wet strength, elongation, and *P* agree with the results of the previous report. The tensile strength increased linearly with Γ while Γ was small, but increased more rapidly at large values of Γ. The relation between *R* and Γ was the same as in the previous report.
Text. Research J. Dec. 1949

Ultrasonic Propagation Rate in Macromolecules

The ultrasonic propagation rate in macromolecules. G. Natta and M. Baccaredda. *J. Polymer Sci.* **3**, 829–33 (Dec. 1949).

The ratio of ultrasonic velocity to polymer density, u/ρ, increases with increasing molecular weight of the paraffin straight chain. In cross-linked compounds with ethyl or methyl groups, the ratio is practically constant. In compounds with larger side-chain radicals (phenyl or hydroxyisobutyl), the ratio decreases with increases in molecular weight. Compressibility is higher for cross-linked polymers.
Text. Research J. Dec. 1949 E. D. Klug

Measuring Dynamic Mechanical Properties

A method of measuring dynamic mechanical properties of rubber-like materials. K. W. Hillier, H. Kolsky, and J. P. Lewis. *J. Applied Phys.* **20**, 227 (Feb. 1949).

A method devised by Hillier, Kolsky, and Lewis is compared with a similar method described by A. W. Nolle, *J. Applied Phys.* **19**, 753–74 (Aug. 1948). Comment on the Hillier-Kolsky-Lewis method is given by A. W. Nolle, *J. Applied Phys.* **20**, 227–8 (Feb. 1949).
Text. Research J. Dec. 1949

Moisture Regain of Silk

The moisture regain of silk. I. Adsorption and desorption of water by silk at 25°C. E. A. Hutton and J. Gartside. *J. Text. Inst.* **40**, T161–9 (Mar. 1949).

A review of earlier work shows varying results obtained by different investigators. The adsorption and desorption isotherms at 25°C were determined for Japanese, Chinese, and Italian silks, both in the gum and after degumming, using the vacuum adsorption apparatus de-

vised by Urquhart and Williams. Good agreement was found between this method and a desiccator method when comparative tests were made on 2 samples of Japanese silks. In the gum state, the adsorption was slightly higher for the Italian silk than for the Japanese and Chinese silks, but after degumming the 3 kinds of silk absorbed water to practically the same extent. The regains were greater at all humidities for the silk in the gum state than for the degummed silk. Considerable hysteresis between the absorption and desorption regain curves was found for all the samples, the differences at 65% R.H. being approximately 1.50% for the gum silk and 1.15% for the degummed material. Attempts to determine the moisture content of the isoelectric sample of degummed Japanese silk were unsuccessful above 80% R.H., probably because of degradation of the isoelectric silk at the higher humidities. Results below about 80% R.H. indicate that the adsorptive capacity of the degummed Japanese silk was slightly reduced when the silk was made isoelectric. The gum contents were approximately 20% for the Japanese and Chinese silks and about 25% for the Italian silk. Approximate values for the regain of sericin at different relative humidities were calculated. R. K. Worner

Text. Research J. Dec. 1949

Sorption of Water by Nylon

The adsorption and desorption of water by nylon at 25°C. E. A. Hutton and J. Gartside. *J. Text. Inst.* **40**, T170–4 (Mar. 1949).

The adsorption-desorption isotherms for type 66 nylon were determined at 25°C, using parachute fabric woven from delustered yarn. A small but definite hysteresis was obtained by both the desiccator and vacuum methods, employed as described in a paper the abstract of which is above. The regain at saturation is approximately 8.70%. The adsorptive capacity of nylon decreased with increasing temperature of drying, but subsequent saturation with water vapor restored the normal affinity for water either completely or to a large extent, depending upon the drying temperature. R. K. Worner

Text. Research J. Dec. 1949

Formaldehyde on Nylon

Preparation and properties of *N*-methylol, *N*-alkoxymethyl and *N*-alkylthiomethyl polyamides. T. L. Cairns, H. D. Foster, A. W. Larchar, A. K. Schneider, and R. S. Schneider. *J. Am. Chem. Soc.* **71**, 651–5 (Feb. 1949).

The preparation and properties of representative examples of *N*-methylol, *N*-alkoxymethyl, and *N*-alkylthiomethyl polyamides by the treatment of linear polyamides with formaldehyde in the presence of acids or bases, or with formaldehyde and alcohols or mercaptans in the presence of acids, respectively, have been described. Authors

Text. Research J. Dec. 1949

Polymer Constitution and Fiber Properties

Polymer constitution and fiber properties. R. Hill and E. E. Walker. *J. Polymer Sci.* **3**, 609–30 (Oct. 1948).

The chemical structure of a large number of linear polycondensation polymers is correlated with ability to form useful fibers. Such factors as the influence of polarity on the linkages, polymer side chains on degree of crystallinity, and melting point are discussed. While this is primarily a review, some new data are included. E. D. Klug

Text. Research J. Dec. 1949

Modulus of Elasticity of Polymers

Statistical calculations and elasticity of high polymers. P. Piganiol. *Inds. plastiques* **4**, 222–4 (1948) (through *Chem. Abstr.* **43**, 438*a* (Jan. 10, 1949)).

A statistical development and experimental data are presented which show that the various links in the chain of a threadlike macromolecule in solution are relatively independent of one another. The results support the hypothesis of Kuhn over the Staudinger theory of rigid, elongated structures, and give a fairly good quantitative idea of the structure of the molecule. It may be shown that the modulus of elasticity (I) varies as the absolute temperature. I is not as dependent upon the chemical structure of the material as has been believed. I varies from 0.6 (plastic sulfur) to 2.4 (chloroprene) (dynes/sq. cm. $\times 10^7$). I is given by an expression of the form $KT\rho = F(M)$, where K is a constant, ρ is the density, and $F(M)$ is a function of the molecular weight which is often taken as equal to $1/M$.

Text. Research J. Dec. 1949

Properties of High Polymers

Constitution and mechanical properties of high polymers. G. Champetier. *Conf. soc. encour. ind. natl.* (France) **3**, 20 pp. (1948) (through *Chem. Abstr.* **43**, 2810*b* (Apr. 10, 1949)).

Discussion of the physical properties of some common natural and synthetic polymers in relation to structure. A "method of small fixed cycle" applied by Chevenard and Champetier (C.A. **40**, 5254[9]) enables the separation of elastic from plastic deformations and follows variations in Young's modulus with elongation. The relative importance of elastic and plastic deformation is discussed for silk, blond hair (keratin) (I), nylon (II), ramie, and rubber (III). Several mechanical analogies are suggested. The purely elastic behavior of II at low elongation is due to a small, reversible deformation of valence angles in the zigzag polymer chains. Further stress causes permanent deformation resulting from slippage of the chains relative to one another. The different behaviors of ramie are correlated with its spiral chain structure. I is intermediate between fibers and III; its elasticity is different from that of III on metals. Thermodynamic relationships in normal and stretched III and chain segment motions (IV) are discussed as well as the lower crystallinity and higher elasticity of the *N*-methyl derivative of II as compared to II. H bonding is diminished and IV increased by

raising the temperature of stretched *I* quickly; this results in a change of fiber to amorphous, highly elastic character. The change is reversed on lowering the temperature. The transformation temperature is lowered by H_2O, $HCONH_2$, or alkaline earth thiocyanates.
Text. Research J. Dec. 1949

Viscosity of Polymers

The behavior of multivalent chain molecules in solution. W. Kuhn, O. Künzle, and A. Katchalsky. *Helv. Chim. Acta* **31**, 1994–2037 (1948) (in German) (through *Chem. Abstr.* **43**, 2487*g* (Apr. 10, 1949)).

The specific viscosity of a very dilute aqueous solution of polymethacrylic acid, having a polymerization number of 650, increases 130-fold when half of the COOH groups are neutralized by alkali. Similar effects of the degree of ionization are observed on the magnitude and orientation of the streaming birefringence and the depolarization of scattered light. These effects are due to the uncoiling of the chain molecules. The molecules are completely stretched when 30–50% of the COOH groups are in the ionized state. This stretching is calculated mathematically in terms of the dependence of the distribution function on the distance between the ends of the molecules as a function of the degree of ionization, α, the degree of polymerization, Z, and the length of a single unit in the chain. The dependence of the specific viscosity on Z changes from the first power for uncharged molecules to the second power for strongly ionized molecules. Expressions are obtained for the dependence of the specific viscosity, sedimentation constant, the magnitude and orientation of the streaming birefringence, and the depolarization of scattered light on Z and α. Good agreement with the observed quantities is obtained. The magnitude of the streaming birefringence depends upon the absolute value of the polarizability of the chain elements. The transition from an uncharged to a charged chain lowers the optical anisotropy in spite of the stretching.
Text. Research J. Dec. 1949

Polymer Solutions

Polymer solutions. H. M. Spurlin. *J. Polymer Sci.* **3**, 714–34 (Oct. 1948).

A qualitative picture of the reasons for the solubility of polymers is given, and the influence of the nature of the polymer and composition of the solvent on solution properties is discussed. E. D. Klug
Text. Research J. Dec. 1949

Properties of Polymer Solutions

Relation of intrinsic viscosity of polymer solutions to degree of polymerization and temperature. C. Sadron. *J. Polymer Sci.* **3**, 812–28 (Dec. 1948).

The relationship $[\eta] = KN^{\alpha}$, where $[\eta]$ is intrinsic viscosity, N is the chain length, and K and α are constants, is analyzed by application of statistics involving the interaction of solute and solvent molecules and the effect of steric hindrance. It is shown that α is a function of N, having a value close to 2 for small values of N and approaching 0.5 for large values of N. Theoretical curves showing effect of temperature are given.
Text. Research J. Dec. 1949 E. D. Klug

Structure of Polyvinyl Alcohol

Occurrence of head-to-head arrangements of structural units in polyvinyl alcohol. P. J. Flory and F. S. Leutner. *J. Polymer Sci.* **3**, 880–90 (Dec. 1948).

The number of head-to-head polymer units in polyvinyl alcohol—*i.e.*, the number of 1,2-glycol units—were measured by treating the sample with periodic acid. Instead of measuring the amount of periodic acid consumed, the more sensitive method of measuring the extent of degradation was employed. Extent of degradation, determined from intrinsic viscosity and osmotic pressure data, indicated that the number of head-to-head polymer units was dependent upon the temperature of polymerization. For polymerization at 25°C, these amounted to 1.23%; for polymerization at 110°C, the value was 1.95%. E. D. Klug
Text. Research J. Dec. 1949

Polyvinyl Chloride

Some curious properties of polyvinyl chloride. J. Delorme. *Inds. plastiques* **4**, 225–31 (1948) (through *Chem. Abstr.* **43**, 435*i*–436*a* (Jan. 10, 1949)).

The values obtained in the determination of the molecular weight of polyvinyl chloride (*I*) by measurement of the viscosity of disperion vary considerably with: solvent used; concentration of *I*; time of heating and temperature of preparing the dispersion; time of storage after dispersion; temperature of determining viscosity. The changes occurring in the viscosity of dispersions of *I* under various conditions of time, and temperature of preparation, concentration of *I*, type of solvent, and treatment before measurement of viscosity are discussed.
Text. Research J. Dec. 1949

"Lilienfeld Rayon"

Evaluation of the Lilienfeld process. P. Eckert and R. Wirén. *Kunstseide u. Zellwolle* **26**, 270–8 (1948); cf. *C.A.* **43**, 2770*b* (through *Chem. Abstr.* **43**, 3195*f* (Apr. 25, 1949)).

Dyeing intensity (with Chicago Blue B and Diamine Green B) is greater for fibers spun in a 50–80% H_2SO_4 bath than in 30–50% H_2SO_4. Dyeing affinity increased with degree of stretch when spun in 70% H_2SO_4. Dyeing increased with increasing after-ripening. Micellar orientation as determined by x-ray diffraction increases sharply in the range 30–50% H_2SO_4 and decreases with increasing after-ripening. The degree of polymerization is only slightly affected by increasing concentration of H_2SO_4 for any given degree of alkali cellulose ripening. Fibers spun in 50% or higher-concentration H_2SO_4 have high luster, while those spun in concentrations below 50% are milky mat owing to the presence of air bubbles after evaporation of free CS_2. Luster increases with increasing stretch. 40 references.
Text. Research J. Dec. 1949

Viscose Absorption

The effect of the carboxyl groups in viscose sheet on the equilibrium absorption of Chrysophenine G. H. A. Standing and J. O. Warwicker. *J. Text. Inst.* **40**, T175–88 (Mar. 1949).

The equilibrium absorption of Chrysophenine G on viscose sheet was found to depend on the ratio of the mass of sheet to the volume of the dye bath. This effect, which was greatest when the concentration of sodium chloride in the dye bath was low, was due to the presence in the viscose sheet of acidic carboxyl groups which resulted in a lowering of the dye-bath *pH*. For dye baths in which the dye concentration and the total cation concentration of the inorganic electrolytes were maintained constant, the equilibrium absorption increased with decreasing dye-bath *pH* and attained a fairly constant value at *pH*'s between 3 and 2. The absorption isotherms of Chrysophenine on viscose sheet were measured under conditions such that the dye-bath *pH*'s were about 6. The theory of the effect of carboxyl groups in viscose sheet on the equilibrium absorption is discussed. Tentativ calculations based on this theory suggest that the number of carboxyl ions which directly affect the equilibrium absorption may be less than the total number of carboxyl groups in the viscose sheet. Authors

Text. Research J. Dec. 1949

Adsorption of Surface-Active Agents by Fibers

Adsorption of surface-active agents by fibers. J. C. Harris. TEXTILE RESEARCH JOURNAL **18**, 669–78 (Nov. 1948).

A review of the published data concerning the preferential adsorption by fibers of the 3 general types of surface-active agents. The adsorption mechanisms for the various fibers are examined. Cotton does not appear to preferentially adsorb anionic or nonionic agents, but adsorbs those cationic in character. Lack of chemically reactive groups probably accounts for its low reactivity. Chemically, wool is highly reactive and adsorbs all 3 types of surface-active agents. The mechanism of adsorption is examined from the viewpoints of micelle formation of the surface-active agent, electrophoretic charge, chemisorption, and chemical reactivity. Considerable work has been accomplished in this general field, but much remains to be accomplished. Although adsorption phenomena are of great interest, equally as valuable would be data concerning the desorption characteristics of these systems, and there are practically no data on this phase of the problem. Author

Text. Research J. Dec. 1949

Effects of Low Temperature

Low temperature properties of textile materials. E. R. Kaswell. *Am. Dyestuff Reptr.* **38**, P127–34 (Feb. 7, 1949).

This is a report on a portion of a research program sponsored by the United States Army Air Forces and conducted by the Textile Division, M.I.T., and the Fabric Research Laboratories, Inc. High-altitude flying, as well as arctic and antarctic military operations, requires a knowledge of the performance of filamentous materials and other high polymers at temperatures as low as −70°F. Previous investigations of parachute suspension lines and their component members under standard humidity and temperature conditions have shown the requisite properties to be: (1) maximum energy absorption, (2) minimum weight and bulk, and (3) minimum shock load to a jumper. Energy absorption may be directly obtained by measuring the area under a load *vs.* % elongation diagram. As the temperature is reduced, the normal thermoplastic polymer becomes increasingly stiff and brittle—*i.e.*, its elongation diminishes while its strength usually increases. This may produce a gain or loss in energy, depending upon changes in shape of the load-elongation diagram and upon whether the loss in elongation is compensated for by the gain in strength. Since polymeric materials, such as nylon, silk, and rayon, creep or deform when subjected to a stress, rate of loading must also be considered. Yarns which have high elongation and energy absorption when tested at slow laboratory rates of speed (pulling jaw speed of 12 in. per min.) may lose appreciable elongation and energy when attenuated at impact speeds of 26 ft. per sec. The combined effect of impact loading and sub-zero temperature may produce enormous changes. Data are presented on the mechanical properties of silk, undrawn, partially drawn, and fully drawn nylon, Fiber A, and Vinyon E when tested under "slow" and impact loading at room temperature and at −70°F. Since in use many of these materials must withstand more than one loading, the effect of repeated mechanical stressing under the above temperature conditions is also discussed. The data are detailed in 12 graphs and 5 tables. C.A.A.

Text. Research J. Dec. 1949

Melting Point

The effect of surface on melting point. H. Reiss and I. B. Wilson. *J. Colloid Sci.* **3**, 551–61 (Dec. 1948).

The macroscopic nature of fusion in extended systems is discussed in detail. In this connection, the experimental significance of the term "melting point" is examined. A relation between the extent of surface and internal pressure is derived. The new relation is to be distinguished from Kelvin's formula, which relates the pressures on either side of a curved surface, although in special cases the two formulas may coincide. A relation of the solid-melt interfacial tension, the solid-gas interfacial tension, and the liquid-gas interfacial tension is derived for the case of equilibrium between solid and melt. Finally, a general relation between melting point and extent of surface is derived and applied to the case of spheres, films, and threads. Authors

Text. Research J. Dec. 1949

Photo-Viscoelasticity

Mathematical theory of photo-viscoelasticity. R. D. Mindlin. *J.*

Applied Phys. **20**, 206–16 (Feb. 1949).

A phenomenological law of optical birefringence, induced by small strain in viscoelastic materials, is formulated and applied to an idealized medium. The resulting optical-stress-time-temperature relations are used in finding conditions under which models made of viscoelastic materials may be employed in the photoelastic method of solving boundary value problems in the linear theory of elasticity. Author

Text. Research J. Dec. 1949

BLEACHING: DYEING: FINISHING

★

Improved Washing Systems

Washing systems greatly improved. D. S. Queen. *Textile World* **99**, 108–10, 204 (June 1949).

Progress in continuous-bleaching machinery has been reflected in a similar advancement in bleachery washing. Closer and more efficient control of washing is possible. New machinery is described.

A. L. Landau

Text. Research J. Dec. 1949

Slasher Operation

Operating the slasher. F. D. Hering. *Textile Bull.* **75**, 51, 52, 54, 55 (May 1949).

The importance of the proper type of subassemblies used in the size vat is stressed. Ribbed immersion rolls are preferred to smooth-faced types because more even penetration of size is achieved. The size in the size vat should be held at the same level at all times, and it is recommended that it be recirculated constantly. The weighting and covering of the squeeze rolls are also discussed. A. L. Landau

Text. Research J. Dec. 1949

Dyestuffs

Copper-containing dyes. E. Krähenbühl. *Textil-Rundschau* **4**, 157–68 (May 1949).

The carboxyl group is considered the mordant-attracting group of dyes. The properties of certain dyes are explained on the basis of their structures. The effects of treatment with copper salts after dyeing on the shade and resistance to light and laundering are discussed. Dyes which incorporate copper in the dye molecule (*o*-amidophenol derivatives) can be applied like direct dyes and are more resistant to light and laundering. Dye procedures are outlined.

Text. Research J. Dec. 1949 J. F. Krasny

Copper-containing dyes. R. Wizinger. *Textil-Rundschau* **4**, 216–19 (June 1949).

Structure and properties of mordant, chrome, and copper dyes are given. The metallic lakes are shown to have a chelate-ring structure, especially in the case of *o*-dihydroxy compounds. *O*-oxyazo compounds are usually too sensitive to acids, but *o-o'*-dioxyazo compounds give very fast chromium and copper complexes. Copper phthalocyanine and cobalt complexes of the condensation products of salicyl aldehyde and similar products with ethylenediamine or *o*-phenylenediamine are also discussed. The latter, although unsuitable as a dye, is an oxygen carrier and was used as such by the Allies during the invasion, obviating the transport of oxygen bombs.

Text. Research J. Dec. 1949 J. F. Krasny

Vat Dyes on Wool

Application of leuco esters of vat dyestuffs to wool. H. Luttringhaus. *Am. Dyestuff Reptr.* **38**, P172–83 (Feb. 21, 1949).

The treatment of wool to give dimensional stability has produced a demand for colors having increased fastness to washing and light. One approach to this problem has been the use of stabilized leuco esters of vat dyes, the stability of which is relatively good and varies with the different types. These water-soluble stabilized esters have much more affinity for animal fibers, such as wool, than they have for the vegetable fibers, such as cotton. While raising the temperature of the dye bath decreases the affinity of these dyes for cotton, their affinity for wool is thereby increased. In fact, these dyes resemble the acid dyes considerably in their dyeing behavior toward wool. Many of the soluble vats exhaust well on wool at pH 7, particularly the anthraquinone types. The indigoids show much less exhaustion but with increasing introduction of negative halogen atoms in the molecule the indigoids and thioindigoids show better exhaustion. Since many of these colors dye better under slightly acid conditions, it is recommended that some ammonium sulfate be added or, under certain conditions, acetic acid. Exhaustion curves are given for 21 dyes and the results obtained with variation of the dyeing procedures are discussed. C. A. A.

Text. Research J. Dec. 1949

Application of Insoluble Dyes

Studies on the application of insoluble dyes. J. Corbiere. *Teintex* **13**, 433–43 (1948) (through *Chem. Abstr.* **43**, 4015*b* (May 25, 1949)).

Detailed discussion of techniques and dye-bath compositions in which all colors, including black, are used. Pictures of equipment are shown.

Text. Research J. Dec. 1949

Dyeing Plastics

The surface-dyeing of plastics. R. Deverell-Smith. *J. Soc. Dyers and Colourists* **65**, 328–32 (July 1949).

In surface-dyeing a plastic, it is necessary to (1) retain the natural surface of the material, (2) prevent surface distortion of the plastic material due to undue softening, subsequent cracking, or crazing, (3) the method of dyeing should be one which is free from industrial hazards of fire risk and toxicity and be simple to apply, (4) dyeing temperatures must be well below the softening point of the plastic, and (5) maximum fastness must be achieved. The procedures are discussed for dyeing plastics of polymethyl methacrylate, cellulose acetate, cellulose nitrate, casein, urea formaldehyde, phenol formaldehyde, polystyrene, nylon, and cross-linked allyl ester polymers.

Text. Research J. Dec. 1949 C. Amick

Raising Fabrics

The raising of dyed fabrics. C. B. Stevens, C. S. Whewell, and H. T. Yegenaga. *J. Soc. Dyers and Colourists* **65**, 280–4 (June 1949).

There is a widely prevalent opinion in the trade that fabrics dyed with certain dyes are more difficult to raise than undyed fabrics or fabrics dyed with other dyes. The results indicate that in general cloth dyed with Neolan dyes is raised more readily than undyed cloth, but when dyed with acid milling dyes, neutral-dyeing acid dyes, direct cotton dyes, mordant dyes, or indigos the susceptibility of the cloth to raising is reduced. Application of equalizing acid dyes produces little change in raising characteristics. While recognizing considerable variations among individual dyes from each group, it is significant that, except in the case of indigo dyeing, the lower the final pH of the dye bath the more easily can dyed fabric be raised. The changes following dyeing are most marked when the cloth is raised wet. Experiments were made on fabrics which had been dyed with: equalizing acid dyes; acid milling dyes; neutral-dyeing acid dyes; direct cotton dyes; premetallized dyes; mordant dyes applied by the afterchrome method, reduced chrome mordant, or aluminum mordant; and indigo.

Text. Research J. Dec. 1949 C. Amick

Ageing Prints

Short ageing processes for the printing of synthetics, silks and wool. A. K. Saville. *Am. Dyestuff Reptr.* **38**, P310–12 (Apr. 4, 1949).

Acetate, acid, and direct color prints require cottage steaming for at least 1 hr. if the best color value and fastness are to be obtained. This paper discusses new developments in short ageing processes which offer the fastness and color value of older cottage-steaming methods, produced more economically in a rapid ager or a tower ager. This is achieved by the choice of an assistant and concentration such that a solution of the color is either present in the printing paste or formed when the aqueous portion of the paste evaporates during drying. Consequently, the color in solution, instead of in the pigment state as in conventional printing, is rapidly and completely fixed during a short ageing. Recipes for printing acetate, nylon, wool, viscose rayon, and silk are included. C.A.A.

Text. Research J. Dec. 1949

Wool Damage in Discharge Printing

Damage to wool in discharge printing with Rongalite. E. Elöd and H. Zahn. *Textil-Praxis* **4**, 27–30 (1949) (through *Chem. Abstr.* **43**, 4015*e* (May 25, 1949)).

In discharge printing of wool, treatment with dithionite causes damage to the fiber. The dithionite reduces the cystine linkages of the wool and at 100°C supercontraction takes place. To obtain a wool more resistant to damage during discharge printing, reduction of wool or hair by dithionite at 40°C is employed, followed by alkylation with alkyl dihalides—*e.g.*, dibromoethane—to produce new cross-linkages with the reduced —SH groups. *Cf.* Brown and Harris, *C. A.* **42**, 2776*e*.

Text. Research J. Dec. 1949

Microscopy in Dyeing and Finishing

Chemical microscopy in dyeing and finishing. G. L. Royer. *Anal. Chem.* **21**, 442–7 (Apr. 1949).

A review with 12 references. The use of the Calco modification of the Hardy microtome is described. There are 48 colored photomicrographs illustrating fiber cross section, the use of optical staining, and polarized light.

A. R. Macormac

Text. Research J. Dec. 1949

Padding

Preliminary study of variables in padding. N. Y. Section A.A.-T.C.C. *Am. Dyestuff Reptr.* **38**, P159–71 (Feb. 21, 1949).

Most of this investigation was devoted to a study of "pick-up," as it is commonly termed in the textile industry. For the purposes of the paper, pick-up is defined as the weight of liquid retained by the cloth leaving the nip divided by the original weight of the dry cloth (times 100 equals % pick-up). The data indicate that at loads above about 200 lb. per lineal in. the pick-up decreases very slowly and, in addition, the horsepower requirements rise very rapidly. While increased pressure increases the extraction of water, the influence of increased pressure on pick-up depends upon the chemical and physical characteristics of the fiber, the construction of the yarn, the construction of the fabric, the presence of chemicals (wetting agents), the effect of temperature, the effect of immersion time in the liquor, the effect of time in the nip, and the nature of the nip. Less pick-up was obtained at high than at low temperatures, and at fast than at slow speeds, although in the latter case the construction of the fabric may influence the carrying through of liquid by mechanical means. Fabrics which wet out easily retain less water if a wetting agent is present, but fabrics which wet out with difficulty retain more water under these conditons. C. A. A.

Text. Research J. Dec. 1949

Resin Finishing

The resin finishing of textile fabrics. R. G. Thomas. *Am. Dyestuff Reptr.* **38**, 413–16 (May 16, 1949).

Since World War I 3 important developments have markedly affected the textile finishing industry: the development of fast colors, the development of synthetic fibers, and the development of synthetic resins. The fabric finisher may be required to produce finishes that would accomplish the following: (1) stabilization against shrinkage or stretch, (2) crush resistance and resilience, (3) improved handle and drape, (4) light-fastness and wash-fastness, (5) resistance to water, (6) resistance to flame, (7) resistance to mildew, (8) resistance to insect attack, (9) resistance to wear and abrasion. Resin finishes have aided in obtaining these effects. The author discusses thermoplastic resins and thermosetting resins, describes the

properties which each imparts to the fabrics, and predicts a good future for resins in textile finishing. *Text. Research J. Dec. 1949* C.A.A.

Phenyl Mercuric Fungicides

Protection of mechanical cloth with phenyl mercurials. P. P. Hopf and E. Race. *Ind. Eng. Chem.* **41**, 820–7 (Apr. 1949).

Phenyl mercurials exert strong bactericidal and fungicidal influence even at low concentrations. Their general use in industry has been retarded by their low solubility and the consequent difficulty of obtaining even applications of sufficient strength on fabrics, and also by the risk of dermatitis from handling. These difficulties have been overcome by the production of a phenyl mercuric salt of 2,2′-dinaphthyl methane-3,3′-disulfonic acid. This salt goes readily into colloidal solution and the colloid breaks irreversibly when dried on the fiber. Thus, it is possible to treat cloth simply and to obtain a fast protection on this cloth. Qualitative and quantitative microbiological tests on cotton and wool are described for this salt (phenyl mercuric Fixtan) and for phenyl mercuric acetate. *Text. Research J. Dec. 1949* Authors

Mothproofing

Modern protection against moths. R. Zinkernagel. *Textil-Rundschau* **4**, 169–82 (May 1949); **4**, 212–16 (June 1949).

The various moths and beetles which attack keratin and their eating habits are discussed. The larvae cannot live on wool which contains no trace of fats and salts. Of several wool-rayon mixtures, one containing 40% wool was attacked most severely. The chemistry of mothproofing agents is discussed briefly. Studies with Mitin FF (J. R. Geigy Co.), a water-soluble urea compound, show it to be satisfactory in ease of application and the protection afforded. There are 2 types of tests for mothproofing agents: tests for preference, during which the larvae of all keratin-eating insects can choose between several fabrics, and tests during which only one kind of fabric is exposed and the damage measured quantitatively. ASTM, AATCC, and Swiss standard methods are discussed. The last uses small areas treated with bait substances to concentrate the attack, thus accelerating the tests and making evaluation easier. 38 references. *Text. Research J. Dec. 1949* J. F. Krasny

Sizes for Nylon

Laboratory evaluation of sizing material for nylon hosiery yarn. H. B. Goldstein. *Am. Dyestuff Reptr.* **38**, P372–3, P377 (May 2, 1949).

It is the function of a size to overcome the inherent properties of a fiber which may cause serious difficulties in manufacturing. The author states that nylon yarn behaves like an elastic band and should be handled as such. If yarn is to be converted satisfactorily into hosiery, certain of the intrinsic yarn properties must be altered with a size. Procedures used in developing a size for nylon are discussed. C.A.A. *Text. Research J. Dec. 1949*

Crease-Resistance

Theory and practice of crease-resistance in textiles. R. W. Moncrieff. *Text. Mercury and Argus* **120**, 935–9 (June 10, 1949); **120**, 966, 969 (June 17, 1949); **120**, 1011, 1013, 1015 (June 24, 1949).

Following an explanation of the theory of why materials become creased, the following specifications are outlined for the attainment of crease-resistant characteristics: (1) use fibers possessing properties of high extensibility and high elasticity, (2) use soft, twisted yarns, (3) use an open fabric construction, and (4) use a weave which reduces the number of interstices. The chemical theory of crease-resistance is outlined, showing that the presence of cross-linkages in molecular chains is responsible for the imparting of this property to fibers. The urea-formaldehyde resin treatment for making cotton crease-resistant is described. L. A. Fiori *Text. Research J. Dec. 1949*

Wool Scouring

The effect of temperature in the scouring of Merino wool on subsequent processes. P. P. Townend and W. Tweedie. *J. Text. Inst.* **40**, T389–98 (June 1949).

The object of this discussion is to demonstrate how the temperature of the scouring liquors affects the behavior of the wool during its conversion into worsted yarn. Three batches of 64's Australian wool were washed by a 4-bowl scour using the same concentration of scouring agent, but with different ranges of temperature. Tests were made for fiber breakage and nep formation during carding, tear in combing, fiber diagram of the tops, and yarn strength after spinning. These revealed that the wool scoured at the lower temperature range suffered considerably less breakage in carding, gave a better tear in combing and a greater mean fiber length in the top. There was no significant difference in neppiness of card web between the lots. For yarn strength, the results were conflicting and it was not possible to relate temperature in scouring to this property of the yarn. L. A. Fiori *Text. Research J. Dec. 1949*

Wrinkle-Resistant Fabrics

Wrinkle resistance of fabrics. I. J. Gruntfest and D. D. Gagliardi. *Ind. Eng. Chem.* **41**, 760–4 (Apr. 1949).

The results of experiments described in this paper show that the wrinkle resistance of a fabric is determined by the extent of its multifilament character and by the ability of the separate fibers of which it is composed to recover from tensile deformation. The extent of multifilament character depends upon the ratio of fiber diameter to fabric thickness. This ratio determines the minimum strain with which a fold may be made. The extent to which the minimum strain is realized depends upon the ease with which the separate fibers can move relative to one another. This is, in turn, regulated by the structure of the fabric, the presence of sizing or lubricating agents, the smoothness of the fiber surface, and the stiff-

ness of the fibers. Selected urea-formaldehyde resins, formaldehyde alone, and glyoxal, which have access to the inside of the fiber, improve the ability of cellulose fibers to recover from deformation and increase their stiffness. Resin deposited on the outside of the fibers impairs the multifilament character, stiffens the fabric, and reduces its ability to recover from folding.

Text. Research J. Dec. 1949 Authors

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

★

Fiber Identification

Chemical fiber identification. III. A. Agster. *Textil-Praxis* **4**, 226–7 (May 1949).

This paper illustrates and describes the microscopical appearance of commonly used fibers. J. F. Krasny

Text. Research J. Dec. 1949

Drafting of Cotton and Rayon Staple

Control during the drafting of cotton and rayon staple fibers by the back rolls. *Textil-Praxis* **4**, 255–7 (June 1949).

Experiments were conducted to determine the best back-roll covering, the best roll-weighting method, and the optimum pressure on the back roll. Elastic plastic covers (Mipolam) on the top rolls, used in conjunction with fluted steel-bottom rolls, with the weight suspended from the center bearing of the top roll, are recommended. The force acting on the back-roll pair during drafting was measured and found to be as high as 1.1 lbs. in some cases; it increases with the draft between the 2 back-roll pairs to about 1.25 lbs., then decreases with further increase of this draft. Finer roving is less efficiently controlled at the same pressure than coarse roving.

Text. Research J. Dec. 1949 J. F. Krasny

Retting of Flax

Retting of flax. F. Tobler. *Textil-Rundschau* **4**, 186–90 (May 1949).

A short review of present knowledge of factors affecting the retting of flax, and a program for future research to be conducted by the E.M.P.A., a Swiss federal institution at St. Gallen. The ease of retting depends on factors such as variety of flax, stem thickness, maturity, seeding procedure, soil, fertilizer (especially those with phosphorus and potash). The mechanics of retting are described. The efficiency of retting systems can be evaluated by the Krais test—completely retted flax dissociates from the ligneous matter when treated with boiling water, cooled, and shaken violently. J. F. Krasny

Text. Research J. Dec. 1949

Properties of Nylon Filaments

Moisture absorption, density and swelling properties of nylon filaments. N. J. Abbott and A. C. Goodings. *J. Text. Inst.* **40**, T232–46 (Apr. 1949).

Experimental data show the dependence on relative humidity of moisture content, density, and dimensions of drawn and undrawn nylon filaments. All experiments were performed at 70°F. There is a marked hysteresis in the primary adsorption-desorption cycle, but little or no hysteresis in subsequent cycles. Pretreatments with water, ethyl alcohol, aqueous solutions of benzoic acid and *m*-cresol affect the moisture regain. A comparison of the regain values from dryness to saturation for drawn and undrawn nylon, previously soaked in water, and for drawn nylon previously soaked in alcohol shows an appreciable difference only in the upper half of the relative humidity range. Densities, determined by a modified flotation method involving centrifugation, are tabulated at different relative humidities for undrawn, drawn, and 1,100-den. monofilament. Apparent densities in water of the first two are also given. On first wetting out with water, both the drawn and undrawn filaments contract in length. This initial contraction was allowed to take place before investigating the effect of relative humidity on swelling. Percentages for longitudinal swelling of filaments thus stabilized are listed, from dryness to saturation. Percent volume swelling is calculated from density data, and percent lateral swelling from longitudinal and volume swelling data. Experimental values for lateral swelling from dryness to saturation are supported by direct approximate measurements of magnified filament images. The longitudinal and lateral swelling percentages in drawn nylon are approximately equal, while the longitudinal swelling in undrawn filament in water is more than 3 times its lateral swelling. The volume of empty space in a nylon filament is calculated from experimental data and evidence is presented to show that the greater portion of the space remains inaccessible to water. Comparisons are made with the results reported by Speakman and Saville and possible explanations are offered for the seeming disagreements. E. Honold

Text. Research J. Dec. 1949

Analysis of Formaldehyde-Treated Fibers

Qualitative determination of formaldehyde treatments on fibers. A. Schaeffer. *Textil-Praxis* **4**, 287–9 (June 1949).

Methods are described in detail for the qualitative determination of formaldehyde, nitrogen, ammonia, urea, sulfur, and melamine resins. The results can be used to identify the type of formaldehyde finish on the fiber. J. F. Krasny

Text. Research J. Dec. 1949

Processing Rayon Cut Staple

Rayon cut staple. Anon. *Platts Bull.* **6**, No. 8, 146–51 (1949).

Processing details, from opening through spinning, of $1\frac{7}{16}$-in. to 3-in. rayon cut staple are outlined. A spin-plan for a plant of 19,000 spindles for 36's yarn from double roving is illustrated. L. A. Fiori

Text. Research J. Dec. 1949

Slashing and Weaving of Acetate

New acetate size improves slashing and weaving performance

Anon. *Rayon and Synthetic Texts.* **30**, 44–5 (July 1949).

The new synthetic sizing agent, Stymer S, is claimed to impart to acetate yarns flexibility, adhesiveness, and abrasion-resistance without undue stiffening. Other advantages reported are: (1) weaving efficiency is increased, (2) static electricity is reduced, (3) number of seconds is reduced, and (4) desizing time is cut. Actual mill data are shown. L. A. Fiori

Text. Research J. Dec. 1949

Element "X" in Nylon

The element "X" in nylon. A. W. Staudt. *Am. Dyestuff Repr.* **38**, P339–42 (Apr. 18, 1949).

The element "X," discovered by the engineers who work on nylon, is the tendency for the nylon fiber or fabric to return to the "heat-set form" when permitted to remain in a relaxed state. Pre-setting the article at a temperature higher than that reached in subsequent manufacturing or customer operations enables the fiber or article to return to this pre-set form when it is relaxed. A hot-roll machine for treating woven nylon fabrics is described. The fabric is passed over a roll heated at 400°–450°F at a speed to give 2–15 seconds of contact. Since the temperature of the treating roll is close to the melting-point of present nylon textile fiber types (482°F), careful control of temperature and time of contact must be exercised but at these temperatures, nylon fabrics can be thoroughly heat-set. The hand obtained from this treatment is different from that obtained from steam or boiling-water settings, being generally softer and fuller and more desirable for underwear and blouse fabrics. C.A.A.

Text. Research J. Dec. 1949

Electron Microscopy of Wool

An electron microscope study of the structure of wool hair. C. J. Gorter and A. L. Houwink. *Mededel. Vezelinst. T.N.O.* **89**, 8 pp. (1948) (in English) (through *Chem. Abstr.* **43**, 4016*i* (May 25, 1949)).

Wool hair scales show no specific structure. After trypsin action a sponge-like interior results while cortical cells show fibrillization. Wool powder shows no particles smaller than 160–200 Å.

Text. Research J. Dec. 1949

Intermediate Woolen Feeding Mechanisms

Woolen carding. Anon. *Platts Bull.* **6**, No. 9, 183–8 (1949).

The various intermediate feeding mechanisms used on woolen cards are described in some detail. Included are also several types of balling machines. Illustrated.

Text. Research J. Dec. 1949 L. A. Fiori

Drawing Frame

3-over-4 drawing. Anon. *Saco-Lowell Bull.* **21**, 1–9 (Apr. 1949).

Described in detail are 2 models of the 3-over-4 drawing frames. The Model DS-1 is suitable for the processing of wool, rayon, other similar fibers, and blends of fibers having a range in staple length from a minimum of $1\frac{1}{2}$ in. to a maximum of 5 in. The Model DS-2 is built primarily for cotton and $1\frac{9}{16}$-in. rayon. Sectional drawings of each unit are shown. L. A. Fiori

Text. Research J. Dec. 1949

New Ebonite Roving Bobbins

The new ebonite bobbins. Anon. *Textile Weekly* **44**, 18, 20 (July 1, 1949).

Manufacturers claim that these molded ebonite roving bobbins increase production, make better roving, and lower costs. Known as "Lorival" bobbins, they are made as one-piece moldings to within very fine limits of a rough, homogeneous material (hard rubber). This material has great shock resistance, does not absorb oil or water, does not split or crack, and has no metal parts. Many other advantages are enumerated.

Text. Research J. Dec. 1949 L. A. Fiori

New Picking Attachment

The Fringe roll. Anon. *Saco-Lowell Bull.* **21**, 31–4 (Apr. 1949).

A newly developed attachment called the "Fringe" roll, consisting of a wire-wound roll, is installed under the bottom feed-roll or under the nose of the evener pedal. It is set forward to $\frac{1}{32}$ in. from the path of the beater, with the points of the wire facing upward towards the edge of the beater blade. This attachment eliminates the tendency towards "plucking" so that the condition of the stock reaching the screens is very uniform and free from lumps and bunches. Tests have shown no possibility of damage to the fibers by the use of this auxiliary roll. It is designed to permit attachment to existing pickers. Illustrated. L. A. Fiori

Text. Research J. Dec. 1949

Spinning Calculations Simplified

Spinning calculations simplified. Part 8. Anon. *Platts Bull.* **6**, No. 8, 151–6 (1949).

Previous charts numbered 1–48 of this series were included in Parts 1–7. Indicated in this chart series, numbered 49–52, are: slubbing, intermediate, and roving frame production in hanks for various spindle speeds and turns per in.; and conversion of speed frame production from hanks to lbs. per spindle per hr. L. A. Fiori

Text. Research J. Dec. 1949

Spinning calculations simplified. Part 9. Anon. *Platts Bull.* **6**, No. 9, 174–6 (1949).

Indicated in this chart series, numbered 53-54, are: draft change gears required for various drafts on ring spinning frames equipped with ordinary and high-drafting arrangements. L. A. Fiori

Text. Research J. Dec. 1949

Treatment of End-Breakage Data

Collection, analysis, and interpretation of end-breakage data in preparation and weaving. G. A. D. Coghlan and J. Perry. *J. Text. Inst.* **40**, P279–88 (Apr. 1949).

Discussion of how end-breakage data may be compiled for prepara-

tion and weaving. A suggested method of recording the observed faults by the use of 2 simple standard forms, and procedures for interpreting final summations by means of plotted graphs are given. The graphs relate end-breakage rate to number of running ends on cross ball warping for both single and double yarn, breakage rate to possible number of looms per weaver, and breakage rate to loom efficiency. L. A. Fiori

Text. Research J. Dec. 1949

Warp Preparation for Weaving

Requirements in warp preparation for automatic weaving. F. C. Sheldon. *J. Text. Inst.* **40**, P263–71 (Apr. 1949).

Following a general discussion of warp-breakage analysis is described the Barker split shedding motion which, according to research carried out on a prototype of this split motion, reduces warp-breakage rate during weaving, particularly with hairy, under-sized, and closely set warps such as poplins and kindred cloths, fabrics made from "Fibro," sheetings, fine linens, and hair cloths. This split motion causes a different timing to be given to each sheet of warp when crossing from top to bottom shed, while still ensuring a suitable shed opening for the passage of the shuttle. This action tends to eliminate the plucking and entanglement of fibers otherwise resulting from the crowded nature of the warp. Illustrated. L. A. Fiori

Text. Research J. Dec. 1949

Warp Breakage

The nature and incidence of warp breakages in automatic weaving. B. J. Brown. *J. Text. Inst.* **40**, P301–16 (Apr. 1949).

This paper discusses the nature and causes of warp breakages. Warp breakages are classified according to causes—such as knots, impurities, chopped ends, abrasion, soft yarn, twisted ends, taped ends, and unknown. Observations made indicate that knots which are not affected by size or sizing technique offer an opportunity to reduce warp-breakage rates. Also discussed are the influences of some weaving conditions, such as weaving-room humidity and warp moisture content, which are generally believed to influence warp breakages. Evidence suggests that warp-break distribution is not seriously influenced by beam moisture content or by weaving-room humidity conditions within the limits of the observations recorded. L. A. Fiori

Text. Research J. Dec. 1949

Warp Breakages in Woolen and Worsted Weaving

Some factors influencing the number of warp breakages in woolen and worsted weaving. D. C. Snowden. *J. Text. Inst.* **40**, P317–30 (Apr. 1949).

The various causes of friction and tension variations are discussed from 3 standpoints: (1) design of the loom mechanism and ancillaries which control the warp threads during weaving; (2) setting and timing of these mechanisms and controls for the avoidance of reediness, stitching, and other such fabric defects; and (3) fabric structure. The discussion of tension effects is supported by references to records of tension variation in an individual warp thread during the weaving cycle of various fabrics. Calculations of the amount the warp may be stretched during shedding and beating-up indicate the importance of considering the points of low extensibility in a yarn, as well as the weak points, when analyzing the results of yarn tests. Friction on the warp yarns and the repetitive shocks of beating-up are factors which reduce the strength of the yarns as they pass from the warp beam into the fabric. L. A. Fiori

Text. Research J. Dec. 1949

Causes and Effects of Warp Breaks

Some causes and effects of warp breaks. J. Baines and J. U. Steiger. *J. Text. Inst.* **40**, P289–300 (Apr. 1949).

The effect of warp breakages on the weaver's work and on the loom efficiency and some technical factors affecting warp breaks are described. Specifically, details are given for calculating weaver's work load, explaining the effect of a varying warp-breakage rate, effect of loom width and cloth construction on warp breaks, and effects of sizing percentage, warp twist, and condition of the loom on warp breaks. It is shown that a size concentration of 6% in the size box gives the best weaving results. L. A. Fiori

Text. Research J. Dec. 1949

Factors Affecting Warp Breakages

The weaving of continuous-filament and long-staple spun yarns. Some factors affecting warp breakages. V. Castle and F. Dawson. *J. Text. Inst.* **40**, P331–52 (Apr. 1949).

Following a list of factors responsible for warp stoppages are presented weaving efficiency studies of nett silk, spun silk, and nylon warps and also efficiency studies of back-winding and warping of nylon. Knot-strength data obtained by use of the single finger, double finger, single weaver's, double weaver's, and reef knots on some continuous-filament and spun yarns are summarized and evaluated according to the type of knot most suitable for the purpose. Also presented are data on the variability of nett silk yarns, and the effect of discharging, weighting, and dyeing on strength and extensibility. L. A. Fiori

Text. Research J. Dec. 1949

Oiling Wool

Olein as wool-oiling agent. R. Leonardsen. *Textilteknik* **7**, 14–16 (1949) (through *Chem. Abstr.* **43**, 3622*c* (May 10, 1949)).

The requirements of a first-class olein used for oiling wool are: good lubricating power, resistance to spontaneous combustion, washing off with soda solution, no unpleasant odor on the wool, liquid at ordinary working temperature, light color, no foreign admixtures, no fatty acids with several double bonds (would lead to spontaneous combustion), forms soap with alkalies. The analytical limits are: total fat at least

99%, H_2O ash, etc., at most 1%; titer 10–17°, saponification number 190–205, acid number 175–195, ester number 2–5, unsaponifiable 2–5%, I number 70–90, thiocyanogen number 75–85; metal less than 0.05%; flash point about 160°. The greatest danger—combustibility—is tested by the Mackey test. To prevent combustion, especially on the damp yarn, removal of the air either by vacuum or an inert gas, or by addition of an antioxidant (not more than 1–2% 2-naphthol), is recommended. For the Nordic countries, sperm oil, available in large quantities, is a satisfactory olein raw material.

Text. Research J. Dec. 1949

Wool Shrinkage

Some aspects of the chemical control of wool shrinkage. J. M. Gould. *Am. Dyestuff Reptr.* **38**, P407–10 (May 16, 1949).

Relaxation shrinkage is the dimensional change which takes place when a fabric is thoroughly wet out after fabrication. This type of shrinkage results from release of strain set up in the fiber during manufacturing operations. This type of shrinkage is minimized by the "sanforizing process" and the "London shrinking" or "sponging" treatments. Another type of shrinkage is the "fulling" or "felting" shrinkage which occurs when a wool fiber is heated in the presence of moisture. This shrinkage is facilitated by mechanical action. Explanations for this type of shrinkage are listed, and the different procedures for reducing or eliminating felting shrinkage are discussed.

Text. Research J. Dec. 1949 C.A.A.

MISCELLANEOUS

★

Blending System

The G-S blending system. Anon. *Saco-Lowell Bull.* **21**, 35–7 (Apr. 1949).

A blender is described which fulfills the functional requirements of the "sandwich" mixing method and also serves as an apparatus suitable for multiple fiber blending.

Text. Research J. Dec. 1949 L. A. Fiori

Color Evaluation

Device for the evaluation of colors in day and artificial light. Anon. *Textil-Rundschau* **4**, 223–4 (June 1949).

A simple device, consisting of 2 adjoining chambers—one containing a fluorescent light with a spectrum similar to that of daylight, and the other, ordinary artificial light—permits simultaneous evaluation of color. J. F. Krasny

Text. Research J. Dec. 1949

Dyehouse Wastes

Developments in the treatment of dyehouse wastes. S. L. Zack. *Sewage Works Eng.* **20**, 129–30 (1949) (through *Chem. Abstr.* **43**, 3621*b* (May 10, 1949)).

Alkaline dye-waste with suspended solids varying from 100 to 3,000 p.p.m. and B.O.D. from 400 to 4,000 p.p.m. was treated by equalization, lime-and-copperas coagulation, settling, and sludge return, removing about 70% B.O.D. and 60% suspended solids. Aftertreatment in a pond increased over-all removal to 91.3% suspended solids and 92.4% B.O.D.

Text. Research J. Dec. 1949

Equation of State

Equation of state for polystyrene. R. S. Spencer and G. D. Gilmore. *J. Applied Phys.* **20**, 502–6 (June 1949).

A simplified van der Waals' equation of state is proposed for polystyrene. The suitability of the equation is shown by compressibility measurements, which are described in detail. L. P. Witnauer

Text. Research J. Dec. 1949

Fiber Structure

The structure of natural and synthetic fibers. H. Staudinger. *Textil-Rundschau* **4**, 3–17 (1949); cf. *Makromol. Chem.* **2**, 228 (1948) (through *Chem. Abstr.* **43**, 3621*c* (May 10, 1949)).

A review with 57 references.

Text. Research J. Dec. 1949

Infrared Spectra

Infrared absorption spectra of some polymers at liquid-helium temperatures. G. W. King, R. M. Hainer, and J. O. McMahon. *J. Applied Phys.* **20**, 559–63 (June 1949).

Infrared absorption spectra have been obtained for polythene, rubber, polystyrene, and polyvinyl chloride at 4°K. For the most part, the changes in the spectra of the polymers on cooling are small. There is some sharpening and improvement in resolution. For one partially crystalline polymer—polyethylene—one band of the doublet at 720 $cm.^{-1}$ becomes very sharp while the other remains unchanged. The authors interpret the bands as CH_2 wagging in a trans- and a cis-configuration of the hydrocarbon chain. L. P. Witnauer

Text. Research J. Dec. 1949

Inhomogeneous Solid

Scattering by an inhomogeneous solid. P. Debye and A. M. Bueche. *J. Applied Phys.* **20**, 518–25 (June 1949).

A detailed discussion of a method for characterizing the inhomogeneous regions in solids is given. The method is based on the scattering power of solids for electromagnetic radiation. Lucite and 2 optical glass samples are investigated, using visible light. L. P. Witnauer

Text. Research J. Dec. 1949

Non-Ionic Compounds

Non-ionic compounds; their employment in the textile industry. J. P. Sisley, translated by P. J. Wood. *Am. Dyestuff Reptr.* **38**, 513–21 (July 11, 1949).

Anion-active and cation-active compounds show increased emulsifying and softening powers when mixed with non-ionic compounds. They are divided into 3 classes, according to their behavior toward water: non-dispersible types, dispersible types, and soluble types. The non-ionic compounds are classified as products obtained by polymerizing ethylene oxide, products obtained by condensation of fatty bodies or their derivatives with ethylene

oxide, and products obtained by condensation of oxy-alkyl-aryl compounds with ethylene oxide. In the textile industry non-ionic compounds are used principally for wetting agents, washing (wool scouring), emulsifying agents (oiling of wool), acid-fulling of cloth, dyeing assistants (leveling), removal of colors from the fiber, improvement of the fastness of dyeings, and softening agents. These are described in considerable detail. About 140 commercial non-ionic materials are listed and their compositions and principal uses given.
Text. Research J. Dec. 1949 C.A.A.

Leather

Recent developments in leather processing. R. E. Hunnam. *J. Soc. Dyers and Colourists* **65**, 336–41 (July 1949).

A brief survey of some of the new ideas in the practice of leather manufacture is given under the following headings: soaking, unhairing, liming, deliming, degreasing, filling, tanning, fat-liquoring, and dyeing. Surface-dyeing dyes are preferred; for suede leather, where complete penetration is necessary, dyeing is done at a higher pH in the presence of ammonia or other alkali. Basic dyes can be made to penetrate efficiently by using them in the presence of cationic agents. Today most leathers are being finished with water pigment finishes based on casein. C. Amick
Text. Research J. Dec. 1949

Filtration of Viscose

The filtration of viscose through quartz. R. S. Neiman. *Tekstil. Prom.* **7**, No. 8, 31–2 (1947) (through *Chem. Abstr.* **43**, 4010*a* (May 25, 1949)).

Quartz particles from 0.55 to 1.25 mm. in diameter were employed in 8-cm. layers for the filtration of viscose solution under a pressure of 2.5 atmospheres. Values of 450 l./sq. m./hr. were obtained. Several filters were used in parallel to prepare the feed to a cellophane machine.
Text. Research J. Dec. 1949

Simplified Sliver Tester

A simplified sliver tester. J. U. Steiger. *J. Text. Inst.* **40**, T253–67 (May 1949).

A machine, designed for simplicity and the avoidance of unusual inaccuracy in manufacture, is described. Variations in the thickness of cotton slivers are mechanically measured and charted. Examples of the use of the machine in detecting sliver faults are given. Illustrated.
Text. Research J. Dec. 1949 L. A. Fiori

Double-Twist Spindles

The principle of double twisting and a review of the literature. G. Dakin and E. J. L. Smart. *J. Text. Inst.* **40**, T268–98 (May 1949).

The aim of this discussion is to trace the development of the double-twist spindle from its inception by a review of the literature, with special reference to the patents which have been filed, of which a comprehensive list is given (86). Literature references also are given (28). The patent list includes United States and foreign numbers, giving name of the patentee, the subject of the patent, and the year; the articles also are from United States and foreign journals. L. A. Fiori
Text. Research J. Dec. 1949

Pneumafil for Spinning Frames

Pneumafil. Anon. *Platts Bull.* **6**, No. 9, 177–80 (1949).

This article describes in detail the standard applications of the Pneumafil individual unit system to new ring spinning frames. Illustrated.
Text. Research J. Dec. 1949 L. A. Fiori

Lay Drive

Dynamic properties of an improved lay drive. W. E. Baltz. *Textil-Rundschau* **4**, 281–2 (June 1949).

The author suggests a device in which springs are used to store energy, thus decreasing the variation in energy consumption during one weaving cycle caused by the lay movement. J. F. Krasny
Text. Research J. Dec. 1949

Weaving Defects

Lessening tight and loose ends in fabrics. H. E. Wenrich. *Rayon and Synthetic Texts.* **30**, 67–8 (June 1949).

This account deals with remedies for defects caused by tight or loose warp ends. A general plan is outlined for the correction of a tight end. L. A. Fiori
Text. Research J. Dec. 1949

Advanced Mill Engineering

Advanced engineering in Swiss Stoffel plant. H. U. Steinmann. *Textile World* **99**, 101–3, 190, 194 (June 1949).

Advanced plant engineering and design of new Swiss mill features 90-ft. span, double-glazed, self-draining skylights, a tunnel system of light and power cables and pipes, over-head material handling, air conditioning, and efficient hot-water heating. A. L. Landau
Text. Research J. Dec. 1949

Market Changes

Impact of market changes on manufacturing. R. Bouvet. *Papers of A.I.T.T.* **4**, 124–9 (June 1949).

The points discussed deal (1) with continuous-filament viscose rayon and its relationship to moisture, and (2) with the effects of tension on fabric physical dimension, and the part played by warping and warp sizing in relation to quality. Such fabric defects as "shiners," rayon cake problems, and copping are also dealt with at some length.
Text. Research J. Dec. 1949 L. A. Fiori

TEXTILE RESEARCH INSTITUTE, INC.

10 EAST 40TH STREET, NEW YORK 16, N. Y.

TELEPHONE: LEXINGTON 2-2196

OFFICERS

A. G. Ashcroft, *President*
Kenneth Wilson, *Vice-President*
Richard T. Kropf, *Treasurer*
D. B. MacMaster, *Secretary*

BOARD OF DIRECTORS

Term Expires 1952	*Term Expires 1951*	*Term Expires 1950*
Norman C. Armitage	F. Eugene Ackerman	A. G. Ashcroft
Andre Blumenthal	Joseph Brant	Robert Burns
Ephraim Freedman	Miles A. Dahlen	W. J. Fullerton
Thomas G. Hawley, Jr.	Bertrand Hayward	J. B. Goldberg
G. P. Hoff	Richard T. Kropf	Henry Herrmann
Jules Labarthe, Jr.	H. Wickliffe Rose	C. H. Masland, II
Donald H. Powers	Leonard Smith	Edward T. Pickard
W. Bailey Sellars	Kenneth Wilson	H. Gordon Smith

EXECUTIVE COMMITTEE

Kenneth Wilson, *Chairman*
A. G. Ashcroft
Andre Blumenthal
J. B. Goldberg
Richard T. Kropf
H. Wickliffe Rose

DEPARTMENT HEADS

John H. Dillon, *Director of Research*
Julian S. Jacobs, *Director of Publications*
James H. Wakelin, *Associate Director of Research*
P. C. Alford, *Administrative Assistant to Director of Research*
K. Lanse Turner, *Assistant to Director of Research, Field Engineer*

RESEARCH ADVISORY COMMITTEE

Miles A. Dahlen, *Chairman*
William D. Appel
A. G. Ashcroft
F. Bonnet
Malcolm E. Campbell
H. M. Chase
Warren E. Emley
J. B. Goldberg
G. P. Hoff
Richard T. Kropf
Brackett Parsons
Hugh S. Taylor
Werner von Bergen
Albert C. Walker

THE TEXTILE FOUNDATION

INDUSTRIAL BUILDING, NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

PUBLICATION OFFICE: KENT, CONNECTICUT

BOARD OF DIRECTORS

Franklin W. Hobbs, *Chairman*
Frank D. Cheney, *Treasurer*
Donald Comer
Charles F. Brannan, *Secretary of Agriculture*
Charles Sawyer, *Secretary of Commerce*
Edward T. Pickard, *Secretary and Assistant Treasurer*

AIMS OF TEXTILE RESEARCH INSTITUTE, INC.

To promote, cultivate, facilitate,
and conduct textile research

AIMS OF THE TEXTILE FOUNDATION

To engage in economic and scientific
research for the benefit of the textile
industries and their allied branches

LANCASTER PRESS, INC., LANCASTER, PA.